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(54) Title: TOPICAL PERSONAL CARE COMPOSITION CONTAINING ALKENYL OR STYRENE END-CAPPED SILICONE GRAFTED COPOLYMER			
(57) Abstract Topical personal care compositions containing aqueous or hydroalcoholic carriers and silicone grafted copolymers with acid-containing monomers characterized by substantially improved or eliminated hydrolysis of the silicone portion of the copolymer are obtained by the selection of specific types of silicone macromers for incorporation into the silicone grafted copolymer. The silicone macromers are selected from the group consisting of alkenyl end-capped silicone macromers and styrene end-capped silicone macromers, and combinations thereof. The silicone macromers are ethylenically unsaturated, polymerizable monomers having a styrene or alkenyl end-capped silicone group covalently bound to the ethylenically unsaturated portion of the monomer via the styrene or alkenyl end-cap.			

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**TOPICAL PERSONAL CARE COMPOSITION CONTAINING ALKENYL
OR STYRENE END-CAPPED SILICONE GRAFTED COPOLYMER**

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TECHNICAL FIELD

This invention relates to topical personal care compositions containing 10 silicone grafted copolymers and an aqueous or hydroalcoholic carrier suitable for application to the skin or hair, wherein the silicone grafted copolymer is soluble or dispersible in the continuous phase of the carrier.

BACKGROUND OF THE INVENTION

The use of silicone grafted copolymers in a wide variety of topical care 15 compositions, e.g. hair and skin care compositions, has become widely known. These polymers are useful for their film forming and adhesive properties, they can be 20 used as adhesive agents in hair sprays, mousse, and lotions, as well as for a wide variety of skin care products such as cosmetics and skin conditioning compositions, wherein their film forming properties are used to smooth the skin or as an aid to deliver other ingredients to the skin. One of the primary benefits of silicone grafted copolymers is that the silicone portions provide improved tactile properties relative 25 to conventional polymers. For example, hair treated with them retains its styled shape in accordance with the wishes of the user, yet feels softer than hair styled with conventional hair styling polymers. Skin treated with silicone grafted polymers feels smoother to the touch than skin treated with conventional polymers.

One of the most desirable and least costly ways to use silicone grafted 30 copolymers is to formulate them into aqueous or hydroalcoholic carriers, wherein the silicone grafted copolymers is soluble in or otherwise stably distributed throughout the aqueous/hydroalcoholic phase. An alternate and also desirable type of composition provides the silicone grafted copolymer solubilized in a nonaqueous solvent, such as cyclomethicone or a hydrocarbon, which is emulsified in the form of droplets distributed throughout the aqueous or hydroalcoholic carrier. Whereas this 35 type of formulation is useful and desirable for many types of products, it is more desirable and less expensive for many other products to use silicone grafted copolymers that are solubilized or stably dispersed in non-emulsified, non-droplet form in the aqueous or hydroalcoholic carrier.

One of the preferred types of silicone grafted copolymers for use in aqueous topical personal care compositions, especially hair spray compositions, contains

acrylic acid monomers and methacryloxy propyl end-capped silicone macromers. It is highly desirable to use acrylic acid monomers because the acid group provides a high degree of polarity which allows the polymer to be soluble or dispersible in water or hydroalcoholic carriers. Other highly polar monomers, such as many cationic 5 monomers, can provide similar solubility to the polymer but tend to be more hygroscopic. This can result in the product becoming sticky during use, particularly during humid conditions. Unfortunately, it has been found that these silicone grafted copolymers tend to hydrolyze in the aqueous or hydroalcoholic products at an undesirably high rate, resulting in separation of the silicone portion from the 10 remainder of the copolymer. Similar copolymers containing the same type of silicone macromer but not containing the acrylic acid monomer do not hydrolyze at such high rates. Therefore, it appears that the hydrolysis problem surprisingly only occurs when the polymer contains an acrylic acid or other acid-containing monomer.

Hydrolysis is of concern since a wide variety of products contain water as the 15 primary or cosolvent for hair styling polymers and other hair and skin care adhesive polymers. It is a particularly concerning issue in view of the current trend toward developing products having high water content and reduced levels of volatile organic compounds (VOC's). Of particular interest is the trend toward regulation of product to contain reduced levels of VOC's, such as the 55% and 80% VOC regulations 20 anticipated or already present in numerous countries. As the trend toward topical personal care products with reduced levels of VOC's continues, VOC-based formulas will be replaced in whole or in part with aqueous and hydroalcoholic formulas.

It is an object of this invention to provide aqueous and hydroalcoholic topical 25 personal care compositions containing silicone grafted copolymers which have improved stability against hydrolysis. It is also an object of this invention to provide compositions as described above which contain acrylic acid or other acid-containing monomers in the silicone grafted copolymer, or which otherwise can provide the product attributes found in such copolymers. It is another object of this invention to provide compositions which meet the above objects and which contain relatively low 30 or zero levels of volatile organic compounds. These and other benefits of the present invention as may be or become apparent to those in the art can be obtained by the invention described below.

Unless otherwise indicated, all percentages are calculated by weight of the 35 total composition and all ratios are calculated on a weight basis. Unless otherwise indicated, ingredient amounts are based on the active level and therefore do not include carriers or by-products that may be included in commercial or otherwise available materials. The present invention may comprise, consist of, or consist

essentially of any of the essential and various optional and/or preferred ingredients and elements described herein. The terms "soluble" and "insoluble" shall refer to the solubility characteristics of a particular ingredient in the composition, unless otherwise specifically indicated. All viscosities and solubilities are determined at 5 25°C, unless otherwise specifically indicated. Also, unless otherwise indicated, all weight percentages of the compositions hereof are based on the total weight of the composition exclusive of any propellant that may be possibly incorporated into the product or otherwise contemplated.

SUMMARY OF THE INVENTION

10 Topical personal care compositions containing aqueous or hydroalcoholic carriers and silicone grafted copolymers characterized by substantially improved or eliminated hydrolysis of the silicone portion of the copolymer can be obtained in accordance with the present invention. It has been found that such compositions can be obtained by combining acid-containing monomers with the selection of specific 15 types of silicone macromers for incorporation into the silicone grafted copolymer. The silicone macromers hereof are selected from the group consisting of alkenyl end-capped silicone macromers and styrene end-capped silicone macromers, and combinations thereof. The silicone macromers are ethylenically unsaturated, polymerizable monomers having a styrene or alkenyl end-capped silicone group 20 covalently bound to the ethylenically unsaturated portion of the monomer via the styrene or alkenyl end-cap.

25 The compositions hereof can be used in a wide variety of topical personal care applications, including hair care, skin care, cosmetics, and personal cleansing compositions. They are especially useful for hair styling products, such as hair sprays, hair lotions, hair tonics, mousses, hair rinses, and shampoos. Other useful, specific product applications include skin care compositions such as skin moisturizers and other skin conditioning compositions, sunscreens, sunless tanning compositions, skin cleansing compositions, anti-acne compositions, topical analgesic compositions, and other drug-containing topical skin compositions. Skin care compositions also 30 include cosmetics.

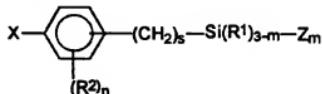
More specifically, the present invention provides topical personal care compositions containing silicone grafted copolymer having improved resistance against hydrolysis, wherein the compositions comprise:

35 (a) from about 0.1% to about 50%, by weight of the composition, of silicone grafted copolymer containing:
(i) from about 1% to about 99%, by weight of the copolymer, of acid-containing monomers, said acids of the acid-containing monomers

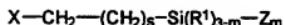
preferably being selected from the group consisting of carboxylic acid and sulfonic acid, and combinations thereof;

(ii) from about 1% to about 50% of silicone macromers having the formula:

5



or



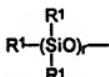
wherein: s is an integer from 0 to about 6; m is an integer from 1 to 3, R² is C1-C10 alkyl or C7-C10 alkylaryl; n is an integer from 0 to 4; X is an ethylenically unsaturated group of the formula:

10



wherein R³ is -H or C1-C6 alkyl; R⁴ is H or C1-C6 alkyl; Z is

15



wherein each R¹ independently is an alkyl, aryl or alkylaryl having from 1 to 10 carbon atoms, and r is an integer from about 4 to about 700, and combinations thereof;

20

(iii) from 0% to about 98% of additional monomers, and combinations thereof; and

25

(b) from about 1% to about 99.9%, by weight of the composition, of an aqueous or hydroalcoholic solvent for said silicone grafted copolymer suitable for application to the hair or skin, wherein said copolymer is soluble or dispersible in said solvent.

The present invention is described in more detail below in the Detailed Description of the Invention.

DETAILED DESCRIPTION OF THE INVENTION

The topical personal care compositions of the present invention generally comprise: (a) from about 0.1% to about 50%, by weight, of the styrene or alkenyl end-capped silicone grafted copolymer hereof, preferably from about 0.2% to about 20%, more preferably from about 0.5% to about 15%, even more preferably from 5 about 1% to about 10%, most preferably from about 2% to about 8%; and (b) from about 1% to about 99.9%, by weight, of an aqueous or hydroalcoholic solvent for the silicone grafted copolymer suitable for application to the hair or skin, preferably from about 50% to about 99.8%, more preferably from about 60% to about 99.5%, even more preferably from about 70% to about 99%, most preferably from about 10 80% to about 98%. The silicone grafted copolymer is soluble or dispersible in the aqueous or hydroalcoholic solvent.

The topical personal care compositions hereof are, by definition, suitable for topical application to the skin or hair. By "suitable for topical application to the skin or hair" what is meant that the compositions are safe for topical application to the 15 skin or hair when used in their intended manner and effective for delivering the copolymers hereof to the skin or hair in such a manner that the copolymer can provide its intended benefit.

Aqueous or Hydroalcoholic Solvent

The aqueous or hydroalcoholic solvent for the copolymers of the present 20 invention can be water or a combination of water and one or more monohydric C1-C6 alcohols, preferably C2-C3 alcohols, more preferably C2 alcohol (i.e., ethanol). The levels of total aqueous or hydroalcoholic solvent are described above. By hydroalcoholic, what is meant is any mixture of water and one or more of the alcohols containing at least about 0.5%, by weight of the solvent, of water.

25 For hair care products in general, such as hair sprays and mousses, however, the compositions hereof will generally comprise at least about 5% water, preferably at least about 10% water, more preferably at least about 20% water.

In another aspect of this invention, the compositions hereof are characterized by reduced levels of volatile organic compounds (VOC's), and will comprise from 30 about 40% to about 99.9% water and from 0% to about 80% of the monohydric alcohols, preferably from 0% to about 55% of the monohydric alcohols. In a particularly preferred embodiment for aerosol or nonaerosol hairspray compositions, the compositions will comprise from about 40% to about 75% water and from about 20% to about 55% monohydric alcohol, or from about 40% to about 95% water and 35 from 0% to about 55% monohydric alcohol. In reduced VOC compositions, the total level of VOC's will preferably be no greater than about 80%, by weight of the composition, inclusive of propellants, preferably no greater than about 55%.

For purposes hereof, VOC's are defined as any organic compounds (including silicones) which either have: a vapor pressure at 20°C of 0.1 mm Hg or higher; or contain 12 or less carbon atoms. Conversely, organic compounds having a vapor pressure of less than 0.1 mm Hg under the same conditions or which contain more than 12 carbon atoms are defined herein as being nonvolatile.

5 The styrene and alkenyl end-capped silicone grafted copolymers hereof are soluble or dispersible in the aqueous or hydroalcoholic solvent. This is in contrast to the situation wherein the copolymer is not soluble or dispersible in the solvent, thereby existing in a separate or discontinuous phase from the solvent.

10 Additional solvents, cosolvents, and solubilizing aids may be incorporated into the compositions hereof to assist with solubilization of the copolymer without departing from the spirit or intent of the invention. Examples of such ingredients include, but are not limited to, di- and tri- hydric alcohols, surfactants and emulsifiers.

15 **Styrene/Alkenyl End-Capped Silicone Grafted Copolymer**

The silicone grafted copolymer (hereinafter sometimes referred to as "the copolymer") constitutes an essential component of the present invention. The term "copolymer", as used herein, refers to polymers derived by polymerization of two or more different species of monomers. The copolymers hereof are made by the 20 copolymerization of one or more types of acid-containing monomers, one or more species of certain styrene or alkenyl end-capped silicone macromers (or a mixture thereof), and optionally one or more other types of monomers. For convenience, the copolymers hereof may sometimes be referred to as being derived from said monomers and macromers, meaning that the copolymer is made by copolymerization 25 of said monomers and macromers. The term "monomer", as used herein, means ethylenically unsaturated compounds capable of being polymerized to form copolymers, as defined herein. The term "macromer", as used herein, shall refer to a monomer characterized by having a polymeric substituent. The essential macromers of the present invention are silicone macromers, meaning that the macromers have 30 silicone as a polymeric substituent. Also, the copolymers hereof may sometimes be said to comprise said monomers and macromers, meaning that the copolymer comprises units corresponding to the indicated pre-polymerization monomers and macromers.

Acid-Containing Monomers

35 The copolymers hereof comprise from about 1% to about 99%, by weight of the copolymer, of acid-containing monomers. In general, the copolymers will preferably comprise from about 5% to about 90%, more preferably from about 10%

to about 80%, most preferably from about 15% to about 75%. The particular level of acid-containing monomer preferred for any specific composition can vary depending on the type of formulation and intended use, as well as the types and amounts of the other monomers and macromers in the copolymer and the molecular weight of the copolymer. For hair spray and other hair care compositions, for example, the copolymer preferably comprises from about 5% to about 50%, by weight of the copolymer, of acid-containing monomer, more preferably from about 10% to about 35%, most preferably from about 15% to about 25%.

The acid-containing monomers will preferably be selected from monomers containing acid groups selected from the group consisting of carboxylic acids and sulfonic acids, most preferably carboxylic acids. Other acid-containing monomers can also be used, including but not limited to phosphonic acid-containing monomers. Combinations of the above types of acid-containing monomers can also be used.

The acid-containing monomer units present in the final copolymer can be derived from polymerizable acid-containing starting monomers, or from polymerizable nonionic monomers which are modified subsequent to polymerization to the acid functionalities. Included within the term acid-containing monomers are the neutralized versions, i.e. salts, of the monomers hereof. Neutralization is discussed in more detail below.

Examples of acid-containing monomers include:

(i) Carboxylic acid-containing monomers, including those corresponding to the formula:



wherein: R⁵ and R⁶ independently are H or C1-C6 alkyl, preferably H or methyl; R⁷ is H, C1-C6 alkyl, or a carboxylic moiety having up to about 12 carbon atoms, preferably H or methyl, or if R⁷ is a carboxylic acid moiety, preferably acrylic acid; and R⁸ is a carboxylic moiety having up to about 12 carbon atoms.

Specific examples of carboxylic acid-containing monomers include acrylic acid, methacrylic acid, maleic acid, maleic acid half ester, itaconic acid, fumaric acid, and crotonic acid, half esters of polybasic acid anhydride such as succinic anhydride, phthalic anhydride or the like reacted with a hydroxyl group-containing acrylate and/or methacrylate such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, and the like.

(ii) Sulfonic acid-containing monomers such as styrenesulfonic acid, and sulfoalkyl acrylates and methacrylates, preferably with C1-C6 alkyl groups, more preferably C2 alkyl groups, such as sulfoethyl acrylate, sulfoethyl methacrylate, and the like.

5 (iii) Phosphoric acid-containing monomers such as the phospho oxyalkyl acrylates and methacrylates, preferably with C1-C6 oxyalkyl groups, more preferably C1-C3 oxyalkyl. Specific examples include phospho-oxyethyl acrylate, phospho-oxyethyl methacrylate, 3-chloro-2-acid phospho-oxypropyl acrylate, phospho-oxypropyl methacrylate, and the like.

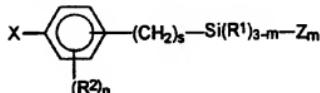
10 Preferred acid containing monomers are the carboxylic acids and the sulfonic acids. Most preferred are the carboxylic acids. Examples of highly preferred acid-containing monomers are acrylic acid, methacrylic acid, and styrenesulfonic acid. Especially preferred acid-containing monomers are acrylic acid and methacrylic acid.

Styrene and Alkenyl End-Capped Silicone Macromers

15 The copolymers hereof comprise from about 1% to about 50%, by weight of the copolymer, of styrene end-capped silicone macromers, alkenyl end-capped silicone macromers, or a combination thereof, preferably from about 2% to about 40%, more preferably from about 5% to about 40%, most preferably from about 5% to about 25%. By "styrene" or "alkenyl" end-capped silicone macromer what is meant is that the macromer contains a silicone, i.e. polymeric siloxane or "polysiloxane" group, that is covalently bound to the monomer via a styrene group or an alkenyl group, respectively.

20 The preferred styrene end-capped silicone macromers and alkenyl end-capped macromers of the present invention have the formulas, respectively:

25



and

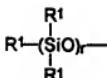


30 wherein: s is an integer from 0 to about 6, preferably 0, 1, or 2, more preferably 0 or 1; m is an integer from 1 to 3, preferably 1; R² is C1-C10 alkyl or C7-C10 alkylaryl, preferably C1-C6 alkyl or C7-C10 alkylaryl, more preferably C1-C2 alkyl; n is an integer from 0 to 4, preferably 0 or 1, more preferably 0; X is an ethylenically unsaturated group (prior to polymerization) of the formula:



wherein R^3 is H or C1-C6 alkyl, preferably H or C1-C2 alkyl, more preferably H; R^4 is H or C1-C6 alkyl, preferably H or C1-C2 alkyl, more preferably H or methyl; Z is:

5



wherein: each R^1 independently is an alkyl, aryl or alkylaryl having from 1 to 10 carbon atoms, preferably C1-C6 alkyl, more preferably C1-C2 alkyl, most preferably methyl; and r is an integer from about 4 to about 700, preferably from about 50 to 10 about 500, more preferably from about 100 to about 300; and combinations thereof. For hair care compositions, such as hair sprays, r is most preferably from about 150 to about 200. The styrene end-capped silicone macromers are preferred.

The silicone portion of the macromer is preferably substituted at the para or meta positions of the aromatic ring relative to X, most preferably at the para position. 15 If n is not 0, then the R^2 group or groups are preferably substituted at the meta positions. The ortho positions are preferably, but not necessarily, unsubstituted.

Styrene and alkenyl end-capped silicone macromers and methods for making them are well-known in the art. See, for example, Holahan, George, Barrie, and Parker, "Monofunctional Polydimethylsiloxane Oligomers For Graft 20 Copolymerization", *Macromol. Chem. Phys.* 195, 2965-2979 (1994), which discloses silicone macromers wherein $s = 0$ for styrene end-capped macromers and wherein and $s = 0$ or an integer for alkenyl end-capped silicone macromers. Further disclosure relating to methods of making the silicone macromers hereof can be found in the Experimental section, below.

25 **Additional Monomers**

The copolymers hereof, in general, comprise from 0% to about 98%, by weight of the copolymer, of additional monomers other than the acid-containing monomers and styrene or alkenyl end-capped silicone macromers described above, preferably from 0% to about 80%, more preferably from 20% to about 70%. For 30 hair care compositions, such as hair sprays, the copolymer preferably comprises from 40% to about 70% of additional monomers. The use of additional monomers can be especially desirable for increasing the T_g of the copolymer, as described in more detail below, or for adjusting the solubility of the copolymer, depending upon the

particular types and levels of the other copolymers and the type and amount of the aqueous or hydroalcoholic solvent. When used in whole or part for one or both of these purposes, the additional monomers will generally be used at a level of at least about 1%, by weight of the copolymer, more generally at least about 2%, preferably at least about 5%, more preferably at least about 10%.

5 A wide variety of the additional monomers can be used. These include nonionic monomers, cationic monomers, and amphoteric monomers. The nonionic monomers can be either low or high polarity monomers. The cationic monomers can be polymerized in the cationic state, or can be polymerized as a nonionic precursor. 10 which is then quaternized or otherwise made cationic subsequent to polymerization. If cationic monomers are to be used, it is preferred that the weight percentage of at least one of either the cationic or acid-containing monomers be no greater than about 10%, preferably no greater than about 5%, to minimize the occurrence of ionic interaction between the two charged groups.

15 Examples of low polarity nonionic monomers are: acrylic and methacrylic acid esters of C1-C24 alcohols, such as methanol, ethanol, allyl alcohol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, oleyl alcohol, isobornyl alcohol, tetrahydrofurfuryl alcohol, and the like, the alcohols preferably having an average number of carbon atoms of from about 1-18, more preferably from about 1-12; 20 styrene; alkylstyrenes, preferably with C1-C6 alkyls, such as t-butylstyrene; chlorostyrene; vinyl esters such as vinyl acetate and vinyl propionate; vinyl chloride; vinyl toluene; vinyl caprolactam; vinylidene chloride; acrylonitrile; alpha-alkylstyrenes, preferably with C1-C6 alkyl groups, such as alpha-methylstyrene; 1,3-dialkenes, such as butadiene and cyclohexadiene; ethylenically 25 unsaturated hydrocarbons, preferably C1-C5 alkenes, such as ethylene and propylene; alkoxyalkyl (meth)acrylates, preferably with C1-C6 alkyl groups, such as methoxy ethyl (meth)acrylate, butoxyethyl (meth)acrylate; and alkyl vinyl ethers, preferably C1-C6 alkyl vinyl ethers, such as methyl vinyl ether. Other low 30 polarity nonionic monomers include: acrylate and methacrylate derivatives such as di-acrylates and di-methacrylates, e.g. ethylene glycol di-acrylate, ethylene glycol di-methacrylate, 1,3-butyleneglycol di-acrylate and -methacrylate; and 35

diacetonaacrylamide. As used herein, the clause "(meth)acrylate" shall mean that both "acrylate" and "methacrylate" are disclosed.

Preferred low polarity nonionic monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

Exemplary high polarity nonionic monomers include; acrylamide; methacrylamide; N,N-dialkyl(meth)acrylamides, especially with C1-C6 alkyls, preferably methyl, such as N,N-dimethylacrylamide; N-alkyl acrylamides, especially with C1-C6 alkyls, such as N-t-butyl acrylamide and isopropylacrylamide; acrylate and methacrylate alcohols, especially C2-C6 (meth)acrylate alcohols, such as hydroxyethyl acrylate, hydroxyethylmethacrylate, hydroxypropylacrylate, and hydroxypropylmethacrylate; vinyl pyrrolidone, allyl alcohol, and vinyl alcohol (made by hydrolyzing vinyl acetate after polymerization).

Cationic monomers include quaternizable, amino-functional, ethylenically unsaturated monomers, such as the amino functional derivatives of styrene, acrylamide, methacrylamide, (meth)acrylates such as the C1-C5 alkyl esters of acrylic acid and methacrylic acid. Preferred are C1-C5 alkyl amines especially C1-C3 amines. It is preferred to use the tertiary amines. (e.g., trialkyl amines), though it is not meant to necessarily exclude monoalkyl amines, dialkyl amines, and other alkyl amine derivatives. Especially preferred are dimethyl amino C1-C3 alkyl amines. These monomers can be quaternized prior to or subsequent to polymerization, preferably subsequent to polymerization.

Cationic monomers include:

(i) monomers derived from acrylic acid or methacrylic acid, which is referred to hereinafter collectively as (meth)acrylic acid, and a quaternarized epihalohydrin product of a trialkylamine having 1 to 5 carbon atoms in the alkyl such as (meth)acryloxypropyltrimethylammonium chloride and (meth)acryloxypropyltriethylammonium bromide;

(ii) amine derivatives of (meth)acrylic acid or amine derivatives of (meth)acrylamide derived from (meth)acrylic acid or (meth)acrylamide and a dialkylalkanolamine having C1-C4 alkyl groups such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, or dimethylaminopropyl (meth)acrylamide; and

(iii) derivatives of the products of the group (ii) above by (1) neutralization with an acid such as hydrochloric acid, or lactic acid, (2) modification with a halogenated alkyl, such as methyl chloride, ethyl chloride, methyl bromide, or

ethyl iodide, (3) modification with a halogenated fatty acid ester such as ethyl monochloroacetate, or methyl monochloropropionate, and (4) modification with a dialkyl sulfate such as dimethyl sulfate, or diethyl sulfate.

Specific examples of such monomers include: (i) p-dimethylaminomethyl 5 styrene, p-dimethylaminoethyl styrene; (ii) dimethylaminomethyl acrylamide, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminomethyl methacrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, and dimethylaminopropyl (meth)acrylamide. Cationic monomers also include amine 10 derivatives of allyl compounds such as diallyldimethylammonium chloride and the like.

As discussed above, cationic monomers can be polymerized in cationic form, or as an alternative they can be polymerized in the form of their precursors, which are then modified to be cationic, for example, by a quaternizing agent (e.g. 15 ethyl monochloroacetate, dimethyl sulfate, etc.).

Examples of the amphoteric monomers include zwitterionized derivatives of the aforementioned amine derivatives of (meth)acrylic acids or the amine derivatives of (meth)acrylamide such as dimethylaminoethyl (meth)acrylate, dimethylaminopropyl(meth)acrylamide by a halogenated fatty acid salt such as 20 potassium monochloroacetate, sodium monobromopropionate, aminomethylpropanol salt of monochloroacetic acid, triethanolamine salts of monochloroacetic acid and the like; and amine derivatives of (meth)acrylic acid or (meth)acrylamide, as discussed above, modified with propanesultone.

These amphoteric monomers, like the aforementioned cationic monomers, 25 can be polymerized in amphoteric form or, as an alternative, they can also be polymerized in the form of their precursors, which are then converted into the amphoteric state.

Copolymers

The copolymers hereof should have a weight average molecular weight of at 30 least about 20,000, for purposes of providing effective adhesive or film forming properties upon application to the hair or skin. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 35 10,000,000, more generally less than about 5,000,000, and preferably less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about

75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000. Molecular weight can be determined by gel permeation chromatography via universal calibration with refractive index and differential viscometric detection using polystyrene standards, or equivalent.

5 Preferably, the copolymer hereof when dried to form a film has a Tg of at least about -20°C, preferably at least about 20°C, so that they are not unduly sticky, or "tacky" to the touch. Preferably, the Tg is from about 20°C to about 120°C. As used herein, the abbreviation "Tg" refers to the glass transition 10 temperature of the non-silicone backbone of the copolymer. Tg can be measured by techniques well known in the art, such as by differential scanning calorimetry (DSC) or dynamic mechanical analysis. Tg can be controlled by varying the level and type of the various acid-containing monomers and additional monomers that are used.

15 Methods for making silicone grafted copolymers have become well-known in the published art. The present silicone grafted copolymers can be made in accordance with known processes, subject to the additional requirement that the starting monomers be chosen such that the final product will be constituted of acid-containing monomers and styrene end-capped silicone macromers as described above. Examples of processes for making silicone grafted polymers are 20 described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference, and also in U.S. Patent 5,061,481, Suzuki et al., issued October 29, 1991, U.S. Patent 5,219,560, Suzuki et al., issued June 15, 1993, U.S. Patent 5,166,276, Hayama et al., issued November 24, 1992, U.S. Patent 25 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, EPO 0 412 707, Torgerson et al., granted February 4, 1994, EPO 0 412 704, Bolich et al., published February 13, 1991, EPO application 92918969.4, Peffly, filed August 18, 30 1992, EPO Application 92918839.9, Hozshuh, et al., filed August 18, 1992, and EPO Application 92919224.3, filed August 18, 1992, all of which are incorporated herein by reference.

35 In general, the copolymers of the present invention can be made by free radical polymerization of silicone macromers with acid-containing monomers and other monomers that may be used. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-

318. The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed.

5 This can be done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved.

10 10 typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The polymer is further purified, as needed.

15 The copolymers hereof will preferably be utilized in at least partially neutralized form. Neutralization can promote solubility or dispersibility of the polymer in the composition. In addition, use of the neutralized form aids in removability of the copolymer from the hair or skin upon cleansing with shampoo, soap, detergent, or other cleansing product. In general, it is preferred that from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about 40% to about 85%, of the acidic functionality of the 20 polymer be neutralized.

25 Any conventionally used base, organic or metallic, may be used for neutralization. Hydroxides of alkali metal and alkaline earth metal are suitable neutralizers for use with the silicone grafted copolymers. Preferred neutralizing agents for use in hair spray compositions of the present invention are potassium hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents which may be used include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), mono-isopropanolamine (MIPA), diisopropanol-amine (DIPA), triisopropanolamine (TIPA) and dimethyl steramine (DMS). Mixtures of amines and bases (metallic or organic) may also be used.

30 Removal of unreacted silicone macromer, if any is present at undesirably high levels which can interfere with product performance, can be done by any means known in the art. One method that can be used is supercritical fluid extraction, such as with supercritical carbon dioxide. Another generally

applicable method is membrane separation, performed in accordance with standard techniques of the art.

A purification method which can be particularly useful for the copolymers hereof is solvent extraction with a nonpolar solvent. Suitable solvents include C3-5 C8 hydrocarbons, preferably C5-C6 hydrocarbons, such as hexane. Before performing the extraction, the polymer reaction product is precipitated out of the reaction solvent (e.g., with water), and dried. The extraction solvent is preferably heated to near or slightly above the average Tg of the non-silicone backbone portion of the polysiloxane-grafted polymer of the adhesive agent. The 10 temperature should be high enough so that the polymer softens, but not so high such that it congeals. The extraction solvent and reaction product can be mixed before, or after heating the solvent. The extraction solvent and polymer reaction product should be held with mixing and preferably in an excess of solvent, for a reasonable period to effectuate removal of the soluble materials. This period will 15 depend upon the reflux temperature of the solvent, the Tg of the copolymer, the temperature to which the solvent is actually heated, the desired level of removal of unreacted monomer and low viscosity material remaining after polymerization, and the number of cycles of solvent extraction to be performed. Typically, the solvent extraction periods will be from about one-half hour to about two hours, 20 more typically from about one-half hour to about one hour. The solvent can be removed after each cycle by conventional means, e.g., decanting, filtering, etc., with drying or distillation to remove trace extraction solvent remaining in the product after the final extraction cycle.

Analysis of the polymer reaction product and the extracted materials, and 25 the purified film-forming agent can be done by conventional analysis techniques known in the art. These include, for example, nuclear magnetic resource (NMR), infrared molecular spectroscopies, gel permeation/size exclusion chromatography, liquid chromatography, gas chromatography, atomic absorption and emission spectroscopies, and wet methods such as titration.

30 Topical Personal Care Compositions

A wide variety of topical personal care compositions are contemplated under 35 the present invention, including both hair care compositions and skin care compositions. Hair care compositions include hair sprays (aerosol and nonaerosol), hair tonics, hair lotions, shampoos, hair rinses, and mousses. Skin care compositions include skin moisturizers and other skin conditioning compositions, sunscreens, sunless tanning compositions, skin cleansing compositions, anti-acne compositions, topical analgesic compositions and other

drug-containing topical skin applications, and the like. Skin care compositions also include cosmetics and fragrances, especially those intended for use in the facial area. Cosmetics include, for example: foundations; eye make-up, such as mascara; and lip make-up. Fragrances include perfumes, colognes, and after-shaves.

5 Topical personal care compositions of the present invention include products wherein the copolymer is used as an adhesive to style hair, to modify the surface of the skin for skin conditioning purposes or for cosmetic appearance purposes. The copolymer hereof can also be used to facilitate delivery of an active ingredient 10 to the hair or skin. Substantivity to the skin or hair can be enhanced for such ingredients as a result of entrapment by the adhesive films the copolymers of the present invention can form upon curing. Examples of such active ingredients include drugs, cosmetic actives (e.g., hair or skin conditioners, dyes and pigments for cosmetics, perfumes and fragrances, and the like), sunscreen actives (including 15 physical sun-blocking actives such as zinc or titanium dioxide, as well as chemical sunscreens which protect the skin or hair by selective absorption of UV-A and/or UV-B rays), and sunless tanning agents.

20 The compositions hereof can be formulated to include any of the ingredients typically known for use in the type of product that is desired, as well as any other 25 ingredients that may provide desireable benefits without interfering unduly with the function of the styrene end-capped silicone grafted copolymer hereof. A nonexclusive description of a variety of such ingredients for use in topical personal care compositions is provided below.

25 The topical personal care compositions can contain a wide variety of volatile materials including, but not limited to acetone, hydrocarbons (such as isobutane, hexane, decene), halogenated hydrocarbons (such as Freons), linalool, esters (such as ethyl acetate, dibutyl phthalate), and volatile silicon derivatives (especially siloxanes such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclo-30 tetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl di-siloxane, cyclomethicones such as octamethyl cyclotetrasiloxane and decamethyl cyclopentasiloxane, and polydimethyl siloxanes, such as dimethicone having, for example, a viscosity at 25°C of about 15 centipoise or less), and mixtures thereof. Volatile materials such as these are commonly used in topical compositions, such as sprays, tonics, gels, and mousses.

35 Aerosol topical personal care compositions, such as mousses and aerosol hair sprays, can utilize any of the conventional propellants to deliver the material. Examples of suitable propellants include materials such as trichlorofluoromethane,

dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane or isobutane. Areosol as well as nonaerosol spray products may include a surfactant to enhance spray quality. Examples of suitable surfactants include nonionic, cationic, anionic surfactants, or mixtures thereof. Fluorosurfactants are also encompassed herein. Surfactants are particularly desirable for the spray product of the present invention, especially spray products such as hair spray, wherein the spray quality can affect product performance, since the compositions hereof have relatively low levels of volatile organic compounds and relatively high levels of water. The high water levels of the present compositions can otherwise adversely affect spray quality. If such a surfactant is used, it is preferably present at a level of from about 0.01% to about 7.5% by weight of the total composition. The level of propellant can be adjusted as desired. It is generally from about 3% to about 30% by total weight of the composition (weight basis inclusive of propellant) of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions. The propellant level in other product forms may vary widely, but is generally between about 3% and about 70%, by weight of the total composition.

Suitable spray containers are well known in the art and include conventional, non-aerosol pump sprays i.e., "atomizers," aerosol containers or cans having propellant, as described above, and also pump aerosol containers utilizing compressed air as the propellant. Pump aerosol containers are disclosed, for example, in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and also in U.S. Serial No. 07/839,648, Gosselin, Lund, Sojka, and Lefebvre, filed February 21, 1992, "Consumer Product Package Incorporating A Spray Device Utilizing Large Diameter Bubbles. Pump aerosols hair sprays using compressed air are also currently marketed by The Procter & Gamble Company under their trademark VIDAL SASSOON AIRSPRAY^R hair sprays.

The compositions of the present invention can be in a wide variety of forms. For example, single phase compositions as well as emulsions wherein the silicone grafted copolymer is present in the aqueous or hydroalcoholic phase of the emulsion. Exemplary emulsions include, but are not limited to, oil-in-water, water-in-oil, water-in-oil-in-water, and oil-in-water-in-silicone emulsions. The silicone grafted copolymer hereof will be present in an aqueous or hydroalcoholic phase of the composition.

The compositions can cover a broad range of viscosities, preferably from about 1 cS to about 200,000 cS, at 25 °C.

Additional Components

A wide variety of additional components can be employed in the topical personal care compositions herein. Non-limiting examples include the following.

Pharmaceutical Actives

The compositions of the present invention can comprise a safe and effective amount of a pharmaceutical active. The phrase "safe and effective amount", as used herein, means an amount of an active high enough to significantly or positively modify the condition to be treated, but low enough to avoid serious side effects (at a reasonable benefit/risk ratio), within the scope of sound medical judgement. A safe and effective amount of the pharmaceutical active will vary with the specific active, 5 the ability of the composition to penetrate the active through the skin, the amount of composition to be applied, the particular condition being treated, the age and physical condition of the patient being treated, the severity of the condition, the duration of 10 the treatment, the nature of concurrent therapy, and like factors.

The pharmaceutical actives which can be used in the compositions of the 15 present invention preferably comprise from about 0.1% to about 20% by weight of the compositions, more preferably from about 0.1% to about 10%, and most preferably from about 0.1% to about 5%. Mixtures of pharmaceutical actives may also be used.

Nonlimiting examples of pharmaceutical actives can include the following:

20 Useful pharmaceutical actives in the compositions of the present invention include anti-acne drugs. Anti-acne drugs preferred for use in the present invention include the keratolytics such as salicylic acid, sulfur, lactic acid, glycolic, pyruvic acid, urea, resorcinol, and N-acetylcysteine; retinoids such as retinoic acid and its derivatives (e.g., cis and trans); antibiotics and antimicrobials such as benzoyl 25 peroxide, octopirox, erythromycin, zinc, tetracyclin, triclosan, azelaic acid and its derivatives, phenoxy ethanol and phenoxy proponol, ethylacetate, clindamycin and mectocycline; sebostats such as flavinoids; alpha and beta hydroxy acids; and bile salts such as scymnol sulfate and its derivatives, deoxycholate, and cholate. Preferred for use herein is salicylic acid.

30 Useful pharmaceutical actives in the compositions of the present invention include non-steroidal anti-inflammatory drugs (NSAIDS). The NSAIDS can be selected from the following categories: propionic acid derivatives; acetic acid derivatives; fenamic acid derivatives; biphenylcarboxylic acid derivatives; and oxicams. All of these NSAIDS are fully described in the U.S. Patent 4,985,459 to Sunshine et al., issued January 15, 1991, incorporated by reference herein. Most preferred are the propionic NSAIDS including but not limited to aspirin, acetaminophen, ibuprofen, naproxen, benoxaprofen, flurbiprofen, fenoprofen, 35

fenbufen, ketoprofen, indoprofen, pirprofen, carprofen, oxaprozin, pranoprofen, miprofen, tioxaprofen, suprofen, alminoprofen, tiaprofenic acid, fluprofen and bucloxic acid. Also useful are the steroidal anti-inflammatory drugs including hydrocortisone and the like.

5 Useful pharmaceutical actives in the compositions of the present invention include antipruritic drugs. Antipruritic drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of methdilazine and trimeprazine. Useful pharmaceutical actives in the compositions of the present invention include include anesthetic drugs. Anesthetic drugs preferred for inclusion 10 in compositions of the present invention include pharmaceutically-acceptable salts of lidocaine, bupivacaine, chlorprocaine, dibucaine, etidocaine, mepivacaine, tetracaine, dyclonine, hexylcaine, procaine, cocaine, ketamine, pramoxine and phenol. Useful pharmaceutical actives in the compositions of the present invention include antimicrobial drugs (antibacterial, antifungal, antiprotozoal and antiviral drugs). 15 Antimicrobial drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of β -lactam drugs, quinolone drugs, ciprofloxacin, norfloxacin, tetracycline, erythromycin, amikacin, triclosan, doxycycline, capreomycin, chlorhexidine, chlortetracycline, oxytetracycline, clindamycin, ethambutol, metronidazole, pentamidine, gentamicin, kanamycin, 20 lineomycin, methacycline, methenamine, minocycline, neomycin, netilmicin, paromomycin, streptomycin, tobramycin, miconazole and amanfadine. Antimicrobial drugs preferred for inclusion in compositions of the present invention include tetracycline hydrochloride, erythromycin estolate, erythromycin stearate (salt), amikacin sulfate, doxycycline hydrochloride, capreomycin sulfate, chlorhexidine 25 gluconate, chlorhexidine hydrochloride, chlortetracycline hydrochloride, oxytetracycline hydrochloride, clindamycin hydrochloride, ethambutol hydrochloride, metronidazole hydrochloride, pentamidine hydrochloride, gentamicin sulfate, kanamycin sulfate, lineomycin hydrochloride, methacycline hydrochloride, methenamine hippurate, methenamine mandelate, minocycline hydrochloride, 30 neomycin sulfate, netilmicin sulfate, paromomycin sulfate, streptomycin sulfate, tobramycin sulfate, miconazole hydrochloride, amanfadine hydrochloride, amanfadine sulfate, triclosan, octopirox, parachlorometa xylene, nystatin, tolnaftate and clotrimazole.

A wide variety of alpha-hydroxy acids and beta-hydroxy acids can be useful for pharmaceutical and cosmetic purposes for the skin, including for anti-aging, reduced dryness, skin exfoliation, and reduction in the appearance of wrinkles and fine lines. These include salicylic acid, glycolic acid, and lactic acid.

Also useful herein are sunscreen agents. A wide variety of sunscreening agents are described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 5,073,372, to Turner et al., issued December 17, 1991; U.S. Patent No. 5,073,371, to Turner et al. issued December 17, 1991; and Segarin, et al., 5 at Chapter VIII, pages 189 et seq., of *Cosmetics Science and Technology*, all of which are incorporated herein by reference in their entirety. Included among those sunscreens are those selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,N-dimethyl-p-aminobenzoate, p-aminobenzoic acid, 2-phenylbenzimidazole-5-sulfonic acid, octocrylene, oxybenzone, homomenthyl 10 salicylate, octyl salicylate, 4,4'-methoxy-1-butylidibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, titanium dioxide, zinc oxide, silica, iron oxide, and mixtures thereof.

Generally, the sunscreens can comprise from about 0.5% to about 20% of the compositions useful herein. Exact amounts will vary depending upon the sunscreen chosen and the desired Sun Protection Factor (SPF). SPF is a commonly used measure of photoprotection of a sunscreen against erythema. See *Federal Register*, Vol. 43, No. 166, pp. 38206-38269, August 25, 1978, which is incorporated herein by reference in its entirety.

Also useful in the present invention are sunless tanning agents including 20 dihydroxyacetone, glyceraldehyde, indoles and their derivatives, and the like. These sunless tanning agents may also be used in combination with the sunscreen agents.

Other useful actives include skin bleaching (or lightening) agents including but not limited to hydroquinone, ascorbic acid, kojic acid and sodium metabisulfite.

Other useful actives which are especially useful for hair care compositions 25 include anti-dandruff actives such as zinc pyrithione, octopirox, selenium disulfide, sulfur, coal tar, and the like.

Zinc pyrithione and triclosan, as well as other anti-bacterials, may also be used in anti-perspirant compositions and deodorant compositions for use on the body, especially in the underarm area.

30 **Conditioners**

The compositions of the present invention can comprise a wide variety of conditioning agents for the hair or skin. The conditioning agents are typically used at a level of from about 0.05% to about 20%, by weight of the composition, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5%.

35 Nonvolatile, as used herein, has the meaning as defined above.

Conditioning agents useful herein, and especially useful for hair care and skin care compositions, include nonvolatile conditioning fluids, such as hydrocarbons, silicone fluids, fatty esters, and fatty alcohols, as well as cationic materials.

5 The conditioning fluids will generally have a viscosity of about 3 million cs or less, preferably about 2 million cs or less, more preferably about 1.5 million cs or less.

10 Conditioning fluids include liquids selected from the group consisting of hydrocarbon oils and fatty esters. The fatty esters include compounds characterized by having at least 10 carbon atoms, and include esters with hydrocarbyl chains derived from fatty acids or alcohols, e.g., mono-esters, polyhydric alcohol esters, and di- and tri-carboxylic acid esters. The hydrocarbyl radicals of the fatty esters hereof can also include or have covalently bonded thereto other compatible functionalities, such as amides and alkoxy moieties (e.g., ethoxy or ether linkages, etc.).

15 Hydrocarbon oils include cyclic hydrocarbons, straight chain aliphatic hydrocarbons (saturated or unsaturated), and branched chain aliphatic hydrocarbons (saturated or unsaturated). Straight chain hydrocarbon oils will preferably contain from about 12 to about 19 carbon atoms, although it is not necessarily meant to be limit the hydrocarbons to this range. Branched chain hydrocarbon oils can and typically may contain higher numbers of carbon atoms. Also encompassed herein are 20 polymeric hydrocarbons of alkenyl monomers, such as C_2-C_6 alkenyl monomers. Specific examples of suitable materials include paraffin oil, mineral oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, and mixtures thereof. A preferred hydrocarbon polymer is polybutene, 25 such as the copolymer of isobutylene and butene. A commercially available material of this type is L-14 polybutene from Amoco Chemical Co. (Chicago, Illinois, U.S.A.).

30 Monocarboxylic acid esters hereof include esters of alcohols and/or acids of the formula $R'COOR$ wherein alkyl or alkenyl radicals and the sum of carbon atoms in R' and R is at least 10, preferably at least 20.

35 Fatty esters include, for example, alkyl and alkenyl esters of fatty acids having aliphatic chains with from about 10 to about 22 carbon atoms, and alkyl and alkenyl fatty alcohol carboxylic acid esters having an alkyl and/or alkenyl alcohol-derived aliphatic chain with about 10 to about 22 carbon atoms, and combinations thereof. Examples include isopropyl isostearate, hexyl laurate, isohexyl laurate, isohexyl palmitate, isopropyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, dihexyldecyl adipate, lauryl lactate, myristyl lactate,

cetyl lactate, oleyl stearate, oleyl oleate, oleyl myristate, lauryl acetate, cetyl propionate, and oleyl adipate. The mono-carboxylic acid ester however need not necessarily contain at least one chain with at least 10 carbon atoms, so long as the total number of aliphatic chain carbon atoms is at least 10. Examples include 5 diisopropyl adipate, diisohexyl adipate, and diisopropyl sebacate.

Di- and tri-alkyl and alkenyl esters of carboxylic acids can also be used. These include, for example, esters of C₄-C₈ dicarboxylic acids such as C₁-C₂₂ esters (preferably C₁-C₆) of succinic acid, glutaric acid, adipic acid, hexanoic acid, heptanoic acid, and octanoic acid. Specific examples include isocetyl stearoyl 10 stearate, diisopropyl adipate, and tristearyl citrate.

Polyhydric alcohol esters include alkylene glycol esters, for example ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol monooleate, polypropylene glycol 2000 15 monostearate, ethoxylated propylene glycol monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol poly-fatty acid esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters are satisfactory polyhydric alcohol esters for use 20 herein.

Glycerides include mono-, di-, and tri-glycerides. More specifically, included are the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids, such as C₁₀-C₂₂ carboxylic acids. A variety of these types of materials can be obtained from vegetable and animal fats and oils, such as castor oil, safflower oil, cottonseed oil, 25 corn oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, lanolin and soybean oil. Synthetic oils include triolein and tristearin glyceryl dilaurate. Preferred glycerides are di-, and tri-glycerides. Especially preferred are triglycerides.

Other conditioning agents fluids include fatty alcohols, preferably C₁₀-C₂₂ alcohols, such as stearyl and cetyl alcohols.

Still other conditioning agents for hair and/or skin include urea; guanidine; aloe vera in any of its variety of forms (e.g., aloe vera gel); polyhydroxy alcohols such as sorbitol, glycerol, hexanetriol, propylene glycol, butylene glycol, hexylene glycol and the like; polyethylene glycols; sugars and starches; sugar and starch derivatives (e.g., alkoxylated glucose); hyaluronic acid; lactamide monoethanolamine; acetamide 30 monoethanolamine; and mixtures thereof.

Silicone Conditioning Agent

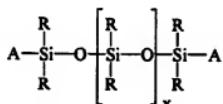
An optional component of the present invention is a nonvolatile, silicone conditioning agent.

The silicone conditioning agent for use herein will preferably have an average viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more 5 preferably from about 10,000 to about 1,800,000, even more preferably from about 100,000 to about 1,500,000. The viscosity of silicones herein can, in general, be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970.

10 The silicone conditioning agent will typically be used in the compositions hereof at levels of from about 0.05% to about 10% by weight of the composition, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 8%, most preferably from about 0.5% to about 5%.

15 Suitable insoluble, nonvolatile silicone conditioning agents include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other insoluble, nonvolatile silicones can also be used. The silicones hereof can be silicone fluids or silicone gums. The term "silicone fluid" shall mean flowable silicone materials having a viscosity of less than 1,000,000 centistokes at 25°C. Generally, the viscosity of the fluid will be between about 5 and 1,000,000 centistokes at 25°C, preferably between about 10 and about 100,000. Silicone 20 gums are described in more detail below.

Silicone fluids hereof include polyalkyl or polyaryl siloxanes with the following structure:



25 wherein R is alkyl or aryl, and x is an integer from about 1 to about 8,000, preferably from about 5 to about 8,000. "A" represents groups which block the ends of the silicone chains.

30 The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the composition, are chemically stable under normal use and storage conditions, and are capable of being deposited on and of conditioning hair.

Suitable A groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicone atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred 5 silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polymethylsiloxane is especially preferred.

The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company in their Viscasil® and SF 96 series, and from Dow 10 Corning in their Dow Corning 200 series.

The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

15 The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified polydimethylsiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide level must be sufficiently low to prevent solubility in water and the composition hereof.

20 Another silicone material that can be especially useful in the silicone conditioning agents is insoluble silicone gum. The term "silicone gum", as used herein, means polyorganosiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described by Petrarch and others including U.S. Patent 4,152,416, Spitzer et al., issued May 1, 1979 and Noll, 25 Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and 30 about 1,000,000. Specific examples include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (di-phenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

Cationic Polymer Hair Conditioning Agent

35 The compositions of the present invention can also comprise cationic polymer conditioning agents. The polymeric cationic conditioning agents hereof will generally be used at levels of from about 0.05% to about 5%, preferably from about 0.1% to about 4%, more preferably from about 0.2% to about 3%, by weight, of the shampoo

composition. The cationic conditioning polymers are preferably water soluble. By "water soluble" cationic organic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. Preferably, the 5 polymer will be sufficiently soluble to form a substantially clear solution at 0.5% concentration, more preferably at 1.0% concentration. The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and up to about 10 million. Preferably, the molecular 10 weight is from about 100,000 to about 2 million. The cationic polymers can generally be characterized by having cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, or a mixture thereof. Any anionic counterions can be utilized for the cationic polymers so long as the water 15 solubility criteria is met. Suitable counterions include halides (e.g., Cl⁻, Br⁻, I⁻, or F⁻, preferably Cl⁻, Br⁻, or I⁻), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other 20 non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl 25 monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C₁-C₇ alkyl groups, more preferably C₁-C₃ alkyl groups. 30 Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the shampoo. In general, secondary and 35 tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines

can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula $R'X$ wherein R' is a short chain alkyl, preferably a C_1 - C_7 alkyl, more preferably a C_1 - C_3 alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

5 Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C_1 - C_3 alkyls, more preferably C_1 and C_2 alkyls.

10 15 Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C_1 - C_7 hydrocarbyls, more preferably C_1 - C_3 , alkyls.

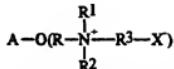
20 25 The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

30 Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, 25 "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallyl ammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallyl ammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and 35 co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include those of the formula:

5



wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual,

10 R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof,

R¹, R², and R³ independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R¹, R² and R³) preferably being about 20 or less, and

15 X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR^R and LR^R series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

25 Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their Jaguar^R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated by reference herein), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated by reference herein).

30 Cationic Surfactant Conditioning Agent

Cationic surfactants useful herein as conditioning agents include quaternary ammonium salts or the salts of fatty amines. Preferred quaternary ammonium salts are dialkyl dimethyl ammonium chlorides, wherein the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids. Representative examples of quaternary ammonium salts include ditallow dimethyl ammonium

chloride, ditallow dimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, and di(hydrogenated tallow) ammonium chloride. Other quaternary ammonium salts useful herein are dicationics such as tallow propane diammonium dichloride. Quaternary imidazolinium salts are also useful herein.

5 Examples of such materials are those imidazolinium salts containing C12-22 alkyl groups such as 1-methyl-1-[(stearoylamide)ethyl]-2-heptadecyl-4, 5-dihydroimidazolinium chloride, 1-methyl-1-[(palmitoylamide)ethyl]-2-octadecyl-4, 5-dihydroimidazolinium chloride and 1-methyl-1-[(tallowamide)-ethyl]-2-tallow-imidazolinium methyl sulfate. Also useful herein are salts of fatty amines. Examples 10 of such compounds include stearylamine hydrochloride, soyamine hydrochloride, and stearylamine formate. Useful conditioning agents are disclosed in U.S. Patent No. 4,387,090, to Bolich, issued June 7, 1983, which is incorporated by reference herein.

Cationic surfactant conditioning agents are generally used at a level of from about 0.1% to about 5%, by weight of the composition.

15 **Surfactants**

Surfactants are optional ingredients in the compositions of the invention. When present, the surfactant typically comprises from about 0.05% to about 50% of the composition. Surfactants are especially useful in cleansing compositions, such as shampoos and skin cleansing compositions, and can be used for a wide variety of 20 other purposes in these and other types of compositions hereof. Exemplary uses include emulsifiers, solubilizers of other ingredients, and conditioning (particularly cationic surfactants. For a shampoo or other cleansing composition, the surfactant level is preferably from about 5% to about 30%, more preferably from 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from 25 about 0.05% to about 5%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, and amphoteric surfactants. A wide variety of surfactants useful herein are disclosed in U.S. Patent No. 5,151,209, to Mc Call et al., issued September 29, 1992; U.S. Patent No. 5,151,210, to Steuri et al., issued September 29, 1992; and U.S. Patent No. 5,120,532, to Wells et al., issued June 9, 1992, all of which are incorporated by reference herein.

Anionic detergents useful herein include alkyl and alkyl ether sulfates. These materials typically have the respective formulae $ROSO_3M$ and $RO(C_2H_4O)_xSO_3M$, wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and 35 triethanolamine.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:

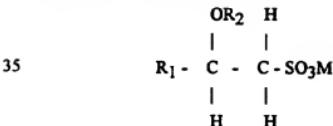


wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the 5 salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C₁₂-10 n-paraffins.

Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of 15 methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants utilizable herein are olefin sulfonates having 25 about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The α -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 30 carbon atoms, preferably about 14 to about 16 carbon atoms. Another class of anionic organic surfactants are the β -alkyloxy alkane sulfonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R_2 is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

5 Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference. Soaps can also be utilized as anionic surfactants.

10 Nonionic surfactants, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of classes of nonionic surfactants are:

15 1. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products.

20 2. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

25 3. Long chain tertiary amine oxides such as those corresponding to the following general formula:



30 25 wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glycerol moiety, and R_2 and R_3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals (the arrow in the formula is a conventional representation of a semipolar bond).

35 30 4. Long chain tertiary phosphine oxides corresponding to the following general formula:



35 wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glycerol moiety and R' and R'' are each alkyl or

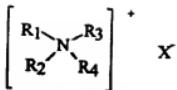
monohydroxylalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond.

5. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-triaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetra decyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

6. N-Polyhydroxy fatty acid amides, such as the polyhydroxyhydrocarbyl C9-C19 fatty acid amides having polyhydroxy functionalities with at least three hydroxy groups, preferably derived from reducing sugars such as glucose, fructose, maltose, lactose, and the like. Surfactants of this type are disclosed in US Patent 2,965,576, E. R. Wilson, issued December 20, 1960, incorporated herein by reference.

Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's Detergents & Emulsifiers (North American edition 1979); Schwartz, et al., Surface Active Agents. Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is generally present at from about 0.05% to about 5%.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R₁-R₄ are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated.

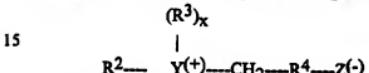
Other quaternary ammonium salts useful herein are diquaternary ammonium salts, such as tallow propane diammonium dichloride.

Quaternary ammonium salts include dialkyldimethyl-ammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein R₁ and R₂ have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutallyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(saturated or unsaturated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropyl diamine, ethoxylated (5 moles

E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbenzylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and 5 stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

10 Amphoteric surfactants, include those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



15 wherein R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

20 25 Other amphoteric such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha carboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) 30 carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the $\text{RCONH}(\text{CH}_2)_3$ radical is attached to the nitrogen atom of the betaine are also useful in this invention.

35 Other examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as

derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

5 Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, sodium 3-dodecylamino propane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold 10 under the trade name "Miranol" and described in U.S. Patent 2,528,378.

Thickening and Suspending Agents

The compositions of the present invention can comprise a wide variety of rheological modifiers as thickening an/or suspending agents. Exemplary ingredients of this type are described below.

15 The compositions may include gel vehicle materials. These are particularly useful for use in products such as hair rinses, creams and lotions.

Gel vehicles can comprise two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail below. Gel vehicles are generally described in the following documents, all 20 incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-25 708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

The carrier may incorporate one or more lipid vehicle materials, regardless of whether it also contains a cationic surfactant, which are essentially water-insoluble, 30 and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

35 Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol

and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

If included in the compositions of the present invention, the lipid vehicle material is typically present at from about 0.1% to about 10.0% of the composition; the cationic surfactant vehicle material is present at from about 0.05% to about 5.0% of the composition.

The use of nonionic cellulose ethers and water-soluble gums for thickening compositions are also contemplated. See for example, U.S. Patent 4,557,928, Glover, issued December 10, 1985, teaching a hair conditioner comprising a suspension system which consists of one of glucan gum, guar gum, and hydroxyethylcellulose; and U.S. Patent 4,581,230, Grollier et al., issued April 8, 1986, which teaches cosmetic compositions for treating hair which comprise as thickening agents hydroxyethylcellulose, or water-soluble vegetable thickening agents, such as guar gum, each incorporated herein by reference.

Cellulose ethers useful for producing viscous compositions include those having a sufficient degree of nonionic substituents selected from the group consisting of methyl, hydroxyethyl, and hydroxypropyl to cause them to be water-soluble and which are further substituted with a hydrocarbon radical having from about 10 to 24 carbon atoms in an amount between about 0.2 weight percent and the amount which renders said cellulose ether less than 1%, by weight, soluble in water. The cellulose ether to be modified is preferably one of low to medium molecular weight; i.e., less than about 800,000 and preferably between about 20,000 and 700,000 (about 75 to 2500 D.P.).

Nonionic water-soluble cellulose ethers are preferred polymers that can be employed in hair care compositions. Widely used, commercially-available nonionic cellulose ethers include methyl cellulose, hydroxy propyl methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose and ethyl hydroxyethyl cellulose.

Other thickening agents for use in the compositions of the present invention, especially for hair rinses, include combinations of hydrophobically-modified polymeric materials with surfactants, such as quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride). These vehicles are described in detail in the following patents: U.S. Patent 5,106,609, issued April 21, 1992 to Bolich et al., U.S. Patent 5,100,658, issued March 31, 1992 to Bolich et al., U.S. Patent 5,104,646, issued April 14, 1992 to Bolich et al., and U.S. Patent 5,100,657, issued March 31, 1992 to Ansher-Jackson et al., each incorporated herein by reference. By "hydrophobically modified nonionic water-soluble polymer" is meant a nonionic water-soluble polymer which has been modified by the substitution with a

sufficient amount of hydrophobic groups to make the polymer less soluble in water. By "water-soluble" what is meant is the polymer or salt, thereof, constituting the polymer backbone of the thickener should be sufficiently soluble such that it forms a substantially clear solution when dissolved in water at a level of 1%, by weight of the solution, at 25°C. Hence, the polymer backbone of the primary thickener can be essentially any water-soluble polymer. The hydrophobic groups can be C₈ to C₂₂ alkyl, aryl alkyl, alkyl aryl groups and mixtures thereof. The degree of hydrophobic substitution on the polymer backbone should be from about 0.10% to about 1.0%, depending on the particular polymer backbone. More generally, the ratio of hydrophilic portion to hydrophobic portion of the polymer is from about 10:1 to about 1000:1.

Nonionic water-soluble cellulose ethers are preferred to be employed as the polymer substrate of these hydrophobically modified polymers. Thus, e.g., hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydroxypropyl methyl cellulose, ethyl hydroxyethyl cellulose, and methyl hydroxyethyl cellulose can be used.

It is also contemplated to utilize a suspending agent to thicken the compositions and/or suspend the insoluble ingredients of the composition. Suitable suspending agents are long chain acyl derivatives, long chain amine oxides, and mixtures thereof, wherein such suspending agents are present in the shampoo compositions in crystalline form. A variety of such suspending agents are described in U.S. Patent Reissue 34,584, Grote et al., issued April 12, 1994. Especially preferred is ethylene glycol distearate.

Also included among the long chain acyl derivatives useful as suspending agents are the N,N-di(hydrogenated) C₈-C₂₂ (preferably C₁₂-C₂₂, more preferably C₁₆-C₁₈) amido benzoic acid, or soluble salt (e.g., K, Na salts) thereof particularly N,N-di(hydrogenated)tallow amido benzoic acid which is commercially marketed by Stepan Company (Northfield, Illinois, USA).

Another component useful in the compositions for thickening or for suspending insoluble ingredients herein is a crosslinked carboxylic polymeric thickener. These crosslinked polymers contain one or more monomers derived from acrylic acid, substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and is derived from a polyhydric alcohol.

Examples of commercially available carboxylic acid polymers include the carbomers, which are homopolymers of acrylic acid crosslinked with allyl ethers of sucrose or pentaerytritol. The carbomers are available as the Carbopol® 900 series

from B.F. Goodrich. Examples of commercially available copolymers also include copolymers of C₁₀₋₃₀ alkyl acrylates with one or more monomers of acrylic acid, methacrylic acid, or one of their short chain (i.e. C₁₋₄ alcohol) esters, wherein the crosslinking agent is an allyl ether of sucrose or pentaerytritol. These copolymers are 5 known as acrylates/C₁₀₋₃₀ alkyl acrylate crosspolymers and are commercially available as Carbopol® 1342, Pemulen TR-1, and Pemulen TR-2, from B.F. Goodrich.

When used, the compositions of the present invention will generally comprise 10 from about 0.01% to about 2%, more preferably from about 0.05% to about 1% and most preferably from about 0.10% to about 0.75% of the carboxylic acid polymer thickeners.

Other thickeners include: low pH thickening agents such as polyacrylamide, available as Sepigel from Seppic Corporation; and crosslinked methyl quaternized dimethylaminomethacrylate, available as Salcare SC95 from Allied Colloids.

15 **Emulsifiers**

The compositions herein can contain various emulsifiers. These emulsifiers are 20 useful for emulsifying the various carrier components of the compositions herein, and are not required for solubilizing or dispersing the copolymers of the present invention. Suitable emulsifiers can include any of a wide variety of nonionic, cationic, anionic, and zwitterionic surfactants as disclosed above and as disclosed in 25 the general literature. See, for example, McCutcheon's, Detergents and Emulsifiers, North American Edition (1986), published by Allured Publishing Corporation; U.S. Patent No. 5,011,681 to Ciotti et al., issued April 30, 1991; U.S. Patent No. 4,421,769 to Dixon et al., issued December 20, 1983; and U.S. Patent No. 3,755,560 to Dickert et al., issued August 28, 1973.

Suitable emulsifiers also include esters of glycerin, esters of propylene glycol, fatty acid esters of polyethylene glycol, fatty acid esters of polypropylene glycol, esters of sorbitol, esters of sorbitan anhydrides, carboxylic acid copolymers, esters and ethers of glucose, ethoxylated ethers, ethoxylated alcohols, alkyl phosphates, 30 polyoxyethylene fatty ether phosphates, fatty acid amides, acyl lactylates, soaps and mixtures thereof.

Suitable emulsifiers also include, but are not limited to, polyethylene glycol 20 sorbitan monolaurate (Polysorbate 20), polyethylene glycol 5 soya sterol, Steareth-20, Ceteareth-20, PPG-2 methyl glucose ether distearate, Ceteth-10, Polysorbate 80, 35 cetyl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, Polysorbate 60, glyceryl stearate, PEG-100 stearate, and mixtures thereof. The emulsifiers can be used individually or as a mixture of two or more and can comprise

from about 0.1% to about 10%, more preferably from about 1% to about 7%, and most preferably from about 1% to about 5% of the compositions of the present invention.

Additional Components

5 The compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable, to improve storage stability and efficacy, or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., colors and dyes, perfumes, pearlescent aids, such as

10 ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonoethanol amide, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl

15 alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; polymer plasticizing agents, such as glycerin, dibutyl

20 adipate, butyl stearate, and propylene glycol; vitamins and derivatives thereof (e.g., ascorbic acid, vitamin E, tocopheryl acetate, retinoic acid, retinol, retinoids, and the like; skin sensates, astringents, skin soothing agents, skin healing agents and the like, nonlimiting examples of these aesthetic components include panthenol and derivatives (e.g. ethyl panthenol), pantothenic acid and its derivatives, clove oil,

25 menthol, camphor, eucalyptus oil, eugenol, methyl lactate, witch hazel distillate, allantoin, bisabolol, dipotassium glycyrrhizinate and the like.); polymers for aiding the film-forming properties and substantivity of the composition (such as a copolymer of eicosene and vinyl pyrrolidone, an example of which is available from GAF Chemical Corporation as Ganex^R V-220); preservatives for maintaining the antimicrobial

30 integrity of the compositions; skin penetration aids such as DMSO, 1-dodecylazacycloheptan-2-one (available as Azone from the Upjohn Co.); and the like. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

35 Method of Using Topical Personal Care Compositions

The compositions of the present invention are used in conventional ways to provide the desired benefit appropriate to the product such as hair styling, holding,

cleansing, conditioning and the like for hair care compositions and benefits such as 5 moisturization, sun protection, anti-acne, anti-wrinkling, artificial tanning, analgesic, and other cosmetic and pharmaceutical benefits for skin care compositions. Such methods of use depend upon the type of composition employed but generally involve application of an effective amount of the product to the hair or skin, which may then be rinsed from the hair or skin (as in the case of shampoos and some conditioning 10 products) or allowed to remain on the hair (as in the case of spray, mousse, or gel products), or allowed to remain on the skin (as in the case of the skin care compositions). By "effective amount" is meant an amount sufficient to provide the benefit desired. Preferably, hair rinse, mousse, and gel products are applied to wet or 15 damp hair prior to drying and styling of the hair. After such compositions are applied to the hair, the hair is dried and styled in the usual ways of the user. Hair sprays are typically applied to dry hair after it has already been dried and styled. Cosmetic and pharmaceutical topical skin care compositions are applied to and rubbed into the skin.

The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

EXPERIMENTAL

Silicone macromers I and II and Polymers I, II, and III, can be synthesized according following procedures. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, 25 reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

Synthesis of 1-(Dimethylchlorosilyl)-2-(p-styryl)ethane End-Cap

In a three neck round bottom flask equiped with a magnetic stirrer, a thermometer 30 and an addition funnel, a solution of divinyl benzene (50.0g, 0.384 moles) and chlorodimethyl silane (11.113 g, 0.128 moles) is prepared in dry tetrahydrofuran (THF) (200 mL). To this solution, a chloroplatinic acid solution (0.150 g in 20 mL THF) is added dropwise. The reaction is highly exothermic, hence a slow addition of chloroplatinic acid is necessary. After the addition of platinic acid, the 35 reaction is allowed to continue for an additional one hour, with stirring. This solution (10.64 M) is used to prepare styrene end-capped silicone macromer I, as described below.

Silicone Macromers I and II: In a round bottom flask which is equipped with a magnetic stirrer, a solution of hexamethylcyclotrisiloxane monomer (150 g) is prepared in dry cyclohexane (150 g). sec-Butyl lithium (0.0125 moles) initiator is added dropwise. The reaction mixture is allowed to stir for 10 minutes. This step 5 is followed by the addition of THF (150 g) to the reaction mixture. The solution is stirred overnight, followed by heating at 50 deg C for 5 hours. The end-cap (0.025 moles) is then added slowly to the solution. Silicone Macromer I is made with the 1-(Dimethylchlorosilyl)-2-(p-styryl)ethane end-cap, as prepared above. The end-cap solution of the above end-cap synthesis is added dropwise. Silicone 10 Macromer II is made with a chlorodimethylstyrylsilane end-cap, which can be prepared as described and shown in Holohan, George, Barrie, and Parker, "Monofunctional Polydimethylsiloxane Oligomers For Graft Copolymerization", Macromol. Chem. Phys. 195, 2965-2979 (1994). The end-cap from this synthesis is added dropwise to the solution. Alternately, the end-cap can be solubilized in 15 THF and then added dropwise. The macromer is recovered by precipitating the final solution in methanol.

Polymer I: Place 20 parts acrylic acid, 63 parts t-butylacrylate, and 17 parts styrene end-capped polydimethylsiloxane macromer(Silicone Macromer I) in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction 20 solvent to produce a final monomer concentration of 25%. Add initiator, azobisisobutyronitrile, to a level of 0.5% by weight relative to the amount of monomer. Purge the flask of oxygen by inserting an argon gas line below the surface of the liquid and allowing argon to bubble into the reaction solvent for about 15 minutes. Heat to 60°C and maintain this temperature for 48 hours while 25 agitating. Terminate the reaction by cooling to room temperature, and dry off the reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

Polymer II: Place 20 parts acrylic acid, 63 parts t-butylacrylate, and 17 parts styrene end-capped polydimethylsiloxane macromer(Silicone Macromer II) in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction 30 solvent to produce a final monomer concentration of 25%. Add initiator, azobisisobutyronitrile, to a level of 0.5% by weight relative to the amount of monomer. Purge the flask of oxygen by inserting an argon gas line below the surface of the liquid and allowing argon to bubble into the reaction solvent for about 15 minutes. Heat to 60°C and maintain this temperature for 48 hours while 35 agitating. Terminate the reaction by cooling to room temperature, and dry off the

reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

Polymer III: Place 20 parts acrylic acid, 30 parts N-isopropylacrylamide, 35 parts t-butylacrylate, and 15 parts styrene end-capped polydimethylsiloxane 5 macromer (Silicone Macromer I) in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction solvent to produce a final monomer concentration of 25%. Add initiator, azobisisobutyronitrile, to a level of 0.5% by weight relative to the amount of monomer. Purge the flask of oxygen by inserting an argon gas line below the surface of the liquid and allowing argon to bubble into the reaction solvent for about 15 minutes. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room 10 temperature, and dry off the reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

EXAMPLES

15 The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ethanol in the following formulas is anhydrous, unless 20 otherwise indicated.

EXAMPLES 1-4

Disclosed below are exemplary mousse compositions of the present invention.

	<u>Component (wt.%)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
5	Polymer III	3.00	3.00	3.00	3.00
	Lauramine-oxide	0.10	0.10	0.00	0.10
	Cocamidopropyl betaine	1.33	1.33	0.30	1.33
	Propylene glycol	0.20	0.10	0.10	0.10
	Perfume	0.10	0.10	0.05	0.10
10	Disodium EDTA - dihydrate	0.10	0.10	0.10	0.10
	Phenoxyethanol	0.25	0.25	0.25	0.25
	Methyl paraben	0.15	0.15	0.15	0.15
	Polyquaternium-41	0.00	0.00	0.00	0.20
	Stearyltrimethylammonium				
15	chloride	0.00	0.00	0.20	0.00
	KOH Solution (45% active)	0.80	0.80	1.00	0.90
	Deionized Water	q.s.	q.s.	q.s.	q.s.

¹Celquat L200, National Starch and Chemical Corp. (Bridgewater, NJ, USA,

20 copolymer of hydroxyethylcellulose and diallyldimethyl ammonium chloride.

The composition is made by mixing the silicone grafted copolymer in the water, with the KOH solution, then sequentially adding the remaining ingredients, except for perfume, with stirring, heating to 40°C - 60°C with stirring, and stirring for an additional period of about eight hours while allowing the composition to cool at ambient temperature, and then mixing in the perfume. The product can then be packaged in a conventional aerosol or non aerosol mousse spray package.

EXAMPLES 5-8

Below are several exemplary reduced VOC hair spray compositions of the present invention.

	<u>Component (wt.%)</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
	Polymer I or II	4.50	3.50	4.00	3.00
	Deionized Water	5.00	3.00	18.00	17.00
	Isododecane	1.50	0.00	0.00	0.00
35	KOH Solution (45% active)	0.90	0.65	0.00	0.75
	NaOH Solution (30% active)	0.00	0.00	1.00	0.00
	Triethyl Citrate	0.20	0.40	0.00	0.10

	Perfume	0.10	0.25	0.05	0.10
	Propylene Glycol	0.05	0.00	0.00	0.10
	N-Butane (Propellant)	7.50	6.00	0.00	0.00
	HFC 152A (Propellant)	15.00	17.00	0.00	0.00
5	Dibutyl Adipate	0.00	0.00	0.30	0.00
	SDA 4 Ethanol	qs	qs	qs	qs

10 The compositions are made by adding the ethanol to a mixing container first, followed by addition of the rest of the non-propellant ingredients sequentially in the order shown above, followed by vigorous stirring for two to three hours. The compositions of Examples 5 and 6 are then added to conventional aerosol cans in the conventional manner and charged with the propellants. The compositions of Examples are added to conventional nonaerosol pump spray containers.

15

EXAMPLE 9

The following is a shampoo composition representative of the present invention.

	Component	Weight %
20	Ammonium laureth sulfate	5.00
	Cocamido propyl betaine	6.00
	Polymer III	4.00
	NaOH Solution (30% active)	0.10
	PEG 150 distearate	2.00
25	Glydant ¹	0.38
	Aminomethylpropanol	0.40
	Perfume	1.00
	Deionized Water	q.s.

¹Preservative commercially available from Glyco, Inc.

30 The shampoo is prepared by combining the ammonium laureth sulfate and Silicone Grafted Copolymer (Polymer III) and heating to 70°C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient temperature. The pH is adjusted to 6.5 by the addition of citric acid or sodium hydroxide, if necessary.

EXAMPLE 10

The following is a styling and conditioning hair rinse composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
5	Polymer III	3.00
	NaOH Solution (30% active)	0.90
	<u>Silicone Premix</u>	
	Silicone Gum GE SE761	0.50
	Decamethyl cyclopentasiloxane	4.00
10	<u>Main Mix</u>	
	Cetyl hydroxyethylcellulose ²	0.60
	Locust bean gum	0.50
	EDTA, disodium salt	0.15
	DTDMAC	0.65
15	Glydant ³	0.40
	Deionized Water	q.s.

¹Commercially available from General Electric

²Polysurf from Aqualon Co.

³Preservative commercially available from Glyco, Inc.

20 The Silicone Premix is blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95°C for 1/2 hour with agitation. As the batch is cooled to about 60°C, the Silicone Premix, Silicone Grafted Copolymer (Polymer III), and NaOH solution are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

25

EXAMPLE 11

Reduced VOC hairspray compositions are prepared from the following components.

<u>Ingredients</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Water	QS 100	QS 100	QS 100	QS 100
Ethanol	54.0	54.0	54.0	54.0
Polymer I, II, or III	4.0	3.0	4.0	3.0
KOH Solution (45% active)	0.80	0.60	1.00	0.75
Diethyl Phthalate	0.40	---	0.10	---
Fragrance	0.05	0.2	---	---

These products are prepared by first dissolving the polymer in the ethanol with stirring. The remaining ingredients are then added with stirring. The resulting hair spray compositions can then be packaged in a nonaerosol spray pump. Alternatively, the compositions can be combined with conventional propellants and packaged in an aerosol spray container.

EXAMPLE 12

Mousse compositions are prepared from the following components utilizing conventional mixing techniques.

10

Ingredients

	<u>Weight %</u>		
	<u>A</u>	<u>B</u>	<u>C</u>
Water	QS 100	QS 100	QS 100
Polymer III	3.00	2.50	3.50
NaOH Solution (30% active)	0.80	0.50	0.90
Lauramide DEA	0.33	0.33	0.33
Sodium Methyl Oleyl Taurate	1.67	1.67	1.67
DMDM Hydantoin	0.78	0.78	0.78
Disodium EDTA	0.20	0.20	0.20
Polyoxyalkylated isostearyl alcohol 1	0.10	0.10	0.10
Fragrance	0.10	0.10	0.10
Propellant 2	7.0	7.0	7.0

These products are prepared by first dissolving the polymer in water with stirring. The remaining ingredients, except the propellant, are then added with stirring. The resulting mousse concentrate can then be combined with conventional propellants (e.g., Propellant A46²) and packaged in an aerosol spray. These mousses are useful for application to the hair to provide a styling and holding benefit.

1 Aerosurf 66-E10.

2 Available as a mixture of 82.46% isobutane, 16.57% propane, and 0.001% butane.

EXAMPLE 13

Hair tonic compositions are prepared from the following components utilizing conventional mixing techniques.

<u>Ingredients</u>	<u>Weight %</u>		
	<u>A</u>	<u>B</u>	<u>C</u>
Ethanol (190 Proof)	QS 100	QS 100	QS 100
Polymer I, II, or III	0.75	1.00	1.25
Aminomethyl Propanol	0.15	0.18	0.22
Fragrance	0.10	0.20	0.30

5 These products are prepared by dissolving the polymer in the ethanol with stirring and then adding the fragrance and any colors. These hair tonics are useful for application to the hair to provide a styling and holding benefit.

EXAMPLE 14

10 A conditioning and styling shampoo composition is prepared from the following components utilizing conventional mixing techniques.

<u>Ingredients</u>	<u>Weight %</u>
<u>Styling Agent</u>	
Polymer III	3.00
15 NaOH Solution (30% active)	0.20
<u>Premix</u>	
Silicone gum	0.50
Dimethicone, 350 cs fluid	0.50
<u>Main Mix</u>	
20 Water	QS100
Ammonium lauryl sulfate	11.00
Cocamide MEA	2.00
Ethylene glycol distearate	1.00
Xanthan Gum	1.20
25 Methylchloroisothiazolinone (and) methylisothiazolinone	0.04
Citric Acid to pH 4.5 as needed	

30 The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main

5 Mix is heated to 150° F with agitation for 1/2 hour. The Styling Agent and the Premix are then added sequentially with about 10 minutes of agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either or both high shear mixing or normal agitation.

EXAMPLE 15

Anti-Acne Composition

An anti-acne composition is made by combining the following components using conventional mixing technology.

	<u>Ingredient</u>	<u>Weight %</u>
10	Water	QS100
	Salicylic Acid	2.00
	Polymer I, II, or III	2.00
15	Ethanol (SDA 40)	40.00
	Aminomethyl Propanol	0.40

EXAMPLE 16

A topical analgesic composition is made by combining the following ingredients utilizing conventional mixing techniques.

	<u>Ingredient</u>	<u>Weight %</u>
20	Water, Purified	QS100
	Ibuprofen	2.00
	Polymer III	2.00
	Aminomethyl Propanol	0.45
25	Ethanol (SDA 40)	20.0 0

EXAMPLE 17

A composition for sunless tanning is made by combining the following ingredients utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
30	<u>Phase A</u>	
	Water	qs 100
	Polymer III	2.00
	NaOH Solution (30% active)	0.70

Carbomer 934 ¹	0.20
Carbomer 980 ²	0.15
Acrylic Acid Copolymer ³	0.15

Phase B

5	PPG-20 Methyl Glucose Ether	
	Distearate	2.00
	Tocopheryl Acetate	1.20
	Mineral Oil	2.00
	Stearyl Alcohol	1.00
10	Shea Butter	1.00
	Cetyl Alcohol	1.00
	Ceteareth-20	2.50
	Ceteth-2	1.00
	Ceteth-10	1.00

15

Phase C

DEA-Cetyl Phosphate	0.75
---------------------	------

Phase D

Dihydroxyacetone	3.00
------------------	------

20

Phase E

Butylene Glycol	2.00
DMDM Hydantoin (and) Iodopropynyl Butylcarbamate	0.25

Phase F

25	Fragrance	1.00
	Cyclomethicone	2.00

In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85^oC. In a separate vessel the Phase B ingredients are combined and heated to 85-90^oC until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The emulsion is cooled to 40-45^oC with continued mixing. Next, in a separate vessel, the dihydroxyacetone is dissolved in water and the

resulting solution is mixed into the emulsion. In another vessel, the Phase E ingredients are heated with mixing to 40-45° C until a clear solution is formed and this solution is then added to the emulsion. Finally, the Phase F ingredients are added to the emulsion with mixing, which is then cooled to 30-35° C, and then to room temperature. This emulsion is useful for topical application to the skin to provide an artificial tan.

5

- 1 Available as Carbopol ^R 934 from B.F. Goodrich.
- 2 Available as Carbopol ^R 980 from B.F. Goodrich.
- 3 Available as Pemulen TR1 from B.F. Goodrich.

10 **EXAMPLE 18**

Sunscreen Composition

An oil-in-water emulsion is prepared by combining the following components utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
15	Phase A	
	Water	QS100
	Carbomer 954 ¹	0.24
	Carbomer 1342 ²	0.16
	Polymer III	1.75
20	NaOH (30%)	0.70
	Disodium EDTA	0.05
	Phase B	
	Isoarachidyl Neopentanoate ³	2.00
	PVP Eicosene Copolymer ⁴	2.00
25	Octyl Methoxycinnamate	7.50
	Octocrylene	4.00
	Oxybenzone	1.00
	Titanium Dioxide	2.00
	Cetyl Palmitate	0.75
30	Stearoxytrimethylsilane (and) Stearyl Alcohol ⁵	0.50
	Glyceryl Tribehenate ⁶	0.75

Dimethicone	1.00
Tocopheryl Acetate	0.10
DEA-Cetyl Phosphate	0.20

Phase C

5	Water	2.00
	Triethanolamine 99%	0.60

Phase D

10	Water	2.00
	Butylene Glycol	2.00
	DMDM Hydantoin (and)	
	Iodopropynyl Butylcarbamate 7	0.25
	dL Panthenol	1.00

Phase E

	Cyclomethicone	1.00
15	1 Available as Carbopol R 954 from B.F. Goodrich.	
	2 Available as Carbopol R 1342 from B.F. Goodrich.	
	3 Available as Elefac I-205 from Bernel Chemical.	
	4 Available as Ganex V-220 from GAF Corporation.	
	5 Available as DC 580 Wax from Dow Corning.	
20	6 Available as Synchrowax HRC from Croda.	
	7 Available as Glydant Plus from Lonza.	

In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85° C. In a separate vessel the Phase B ingredients (except DEA-Cetyl Phosphate) are combined and heated to 85-90° C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The Phase C ingredients are combined until dissolved and then added to the emulsion. The emulsion is then cooled to 40-45° C with continued mixing. In another vessel, the Phase D ingredients are heated with mixing to 40-45° C until a clear solution is formed and this solution is then added to the emulsion. Finally, the emulsion is cooled to 35° C and the Phase E ingredient is added and mixed. This emulsion is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE 19Facial Moisturizer

A leave-on facial emulsion composition is prepared by combining the following components utilizing conventional mixing techniques.

	<u>Ingredient</u>	<u>Weight %</u>
5	Water	QS100
	Polymer III	1.00
	NaOH Solution (30% active)	0.40
	Glycerin	3.00
10	Cetyl Palmitate	3.00
	Cetyl Alcohol	1.26
	Quaternium-22	1.00
	Glyceryl Monohydroxy Stearate	0.74
	Dimethicone	0.60
15	Stearic Acid	0.55
	Octyldodecyl Myristate	0.20
	Carbomer 1342	0.125
	Tetrasodium EDTA	0.10
	DMDM Hydantoin and Iodopropynyl	
20	Butyl Carbamate	0.10
	Carbomer 951	0.075

25

WHAT IS CLAIMED IS:

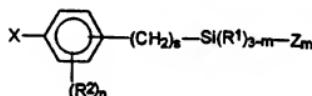
52

1. A topical personal care composition containing silicone grafted copolymer having improved resistance against hydrolysis, said composition being suitable for topical application to the skin or hair, and comprising:

(a) from 0.1% to 50%, by weight of the composition, of silicone grafted copolymer containing:

(i) from 1% to 99%, by weight of the copolymer, of acid-containing monomers;

(ii) from 1% to 50%, by weight of the copolymer, of styrene end-capped or alkene end-capped silicone macromer having the formulas, respectively:



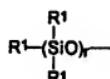
or



wherein: s is an integer from 0 to 6; m is an integer from 1 to 3, R² is C1-C10 alkyl or C7-C10 alkylaryl; n is an integer from 0 to 4; X is an ethylenically unsaturated group of the formula:



wherein R³ is -H or C1-C6 alkyl; R⁴ is H or C1-C6 alkyl; Z is



wherein each R¹ independently is an alkyl, aryl or alkylaryl having from 1 to 10 carbon atoms, and r is an integer from 4 to 700; and combinations thereof;

(iii) from 0% to 98% of additional monomers; and combinations thereof, and

(b) from 1% to 99.9%, by weight of the composition, of an aqueous or hydroalcoholic solvent for said silicone grafted copolymer suitable for application to the hair or skin, wherein said copolymer is soluble or dispersible in said solvent.

2. A composition as in Claim 1, wherein said silicone macromer is the styrene end-capped silicone macromer, n is 0, and said $-(CH_2)_s-Si(R^1)_{3-m}Z_m$ of said silicone macromer is substituted at the para position relative to X wherein s is from 0 to 2, m is 1, n is 0, R³ is H, R⁴ is H or CH₃, and R¹ is an alkyl, preferably wherein R¹ is methyl and r is from 50 to 500.

3. A composition according to any preceding Claim wherein said copolymer comprises from 1% to 50%, by weight of the copolymer, of said additional monomers, said additional monomers being nonionic, cationic, amphoteric, or a combination thereof, preferably wherein said additional monomers are nonionic monomers selected from the group consisting of acrylic and methacrylic acid esters of C1-C24 alcohols; styrene; alkylstyrenes; chlorostyrene; vinyl esters; vinyl chloride; vinyl toluene; vinyl caprolactam; vinylidene chloride; acrylonitrile; alpha-alkylstyrenes; 1,3-dialkenes; ethylenically monounsaturated hydrocarbons; alkoxyalkyl (meth)acrylates; alkyl vinyl ethers; di-acrylates and di-methacrylates; acrylamide; methacrylamide; diacetonaacrylamide; N,N-dialkyl(meth)acrylamides; N-alkyl(meth)acrylamides; acrylate and methacrylate alcohols; vinyl pyrrolidone; allyl alcohol; vinyl alcohol; and combinations thereof.

4. A composition according to any preceding Claim wherein said acid-containing monomers are selected from the group consisting of carboxylic acids and sulfonic acids.

5. A composition as in any preceding Claim wherein said acid-containing monomers are carboxylic acids.

6. A composition as in any preceding Claim wherein said carboxylic acid monomers are selected from the group consisting of those corresponding to the formula:



wherein: R⁵ and R⁶ independently are H or C1-C6 alkyl; R⁷ is H, C1-C6 alkyl, or a carboxylic moiety having up to 12 carbon atoms; and R⁸ is a carboxylic moiety having up to 12 carbon atoms; and mixtures thereof.

7. A composition as in any preceding Claim wherein said copolymer comprises:

- (i) from 5% to 90%, by weight of said copolymer, of said acid-containing monomers;
- (ii) from 2% to 40%, by weight of said copolymer, of said silicone macromers;
- (iii) from 0% to 70%, by weight of said copolymer, of said additional monomers.

8. A composition as in any preceding Claim wherein said copolymer comprises:

- (i) from 10% to 75%, by weight of said copolymer, of said acid-containing monomers;
- (ii) from 5% to 40%, by weight of said copolymer, of said silicone macromers;
- (iii) from 5% to 70%, by weight of said copolymer, of said additional monomers.

9. A composition as in any preceding Claim wherein said copolymer comprises:

- (i) from 15% to 50%, by weight of said copolymer, of said acid-containing monomers;
- (ii) from 5% to 25%, by weight of said copolymer, of said monomers derived from said silicone monomers;
- (iii) from 40% to 70%, by weight of said copolymer, of said additional monomers.

10. A hair spray product comprising the composition of any preceding Claim disposed within an aerosol or nonaerosol spray container.

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.
PCT/US 96/04183A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K/66 AG1K/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 412 770 (MINNESOTA MINING & MFG) 13 February 1991 see claims 1-7 see page 4, line 55 - page 5, line 11 see page 5, line 55 - page 6, line 2 ---	1,3,4
X	WO,A,95 00108 (PROCTER & GAMBLE ;WELCH ROSEMARY JANE (GB); MARCHANT PHILIP JOHN () 5 January 1995 see claims 1-6 ---	1-7
A	WO,A,95 04518 (PROCTER & GAMBLE) 16 February 1995 see claim 1 see page 7, line 23 - page 10, line 25 ---	1,3-6
A	WO,A,93 23446 (PROCTER & GAMBLE) 25 November 1993 -----	

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No
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(54) Title: PERSONAL CARE COMPOSITIONS COMPRISING AN ADHESIVE COPOLYMER	
(57) Abstract	
<p>The present invention relates to personal care compositions. These compositions comprise an adhesive copolymer and a solvent for the copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, acetone, propylene glycol, and mixtures thereof. The compositions, when dried, exhibit a cohesive strength of greater than about 0.5 kgf/mm², a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm³, and an impact strength of greater than about 7000 ergs. Preferred air hairspray embodiments of the present invention having improved removeability from hair as defined by a hair stiffness value of from 0 to about 3.5 (0 to 4 scale) and a hair flaking value of from 0 to about 3.5 (0 to 4 scale), which values are determined by the removeability methodology defined herein.</p>	

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PERSONAL CARE COMPOSITIONS COMPRISING AN ADHESIVE COPOLYMER

TECHNICAL FIELD

The present invention relates to personal care compositions, especially to hair spray compositions having improved removeability from hair as defined by hair stiffness and flaking values. These compositions comprise an adhesive copolymer and a solvent for the copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, acetone, propylene glycol, and mixtures thereof. The copolymer component, when dried, exhibits a cohesive strength of greater than about 0.5 kgf/mm², a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm³, and an impact strength of greater than about 7000 ergs.

BACKGROUND OF THE INVENTION

Personal care products play an important role in the life of most consumers. Personal care products cover a wide variety of products and forms and include shampoos, soaps, hair sprays, lotions, creams, antiperspirants, anti-acne products, nail enamels, lipsticks, foundations, mascaras, and sunscreens. Consumers are constantly seeking personal care products that provide the desired benefit sought and represent a good value.

Many personal care products use contain various resins, gums, and adhesive polymers. The polymers are used for a variety of purposes including thickening, feel properties, film-forming ability, active deposition, active penetration, hair holding, etc. Consequently there is constantly a search for developing polymers having improved properties for use in personal care products.

It has surprisingly been found in the present invention that adhesive copolymers having certain physical parameters are highly useful. These copolymers are used in combination with a solvent for the copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof. The copolymer solvent mixtures, when dried, have a cohesive strength of greater than about 0.5 kgf/mm², a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm³, and an impact strength of greater than about 7000 ergs. Without being limited by theory, it is believed that these physical characteristics of the dried hair spray composition account for the benefits observed.

It has also been found that the preferred hair spray compositions of the present invention have an improved removeability from hair during shampooing, wherein the removeability is defined in terms of hair stiffness and hair flaking values ranging from 0

to about 3.5 (0 to 4 scale). These hair stiffness and flaking values are indirect measures of hair spray removeability. Each of these values are determined in accordance with the methodology defined herein.

It is therefore an object of this invention to provide personal care compositions comprising an adhesive copolymer and a solvent for the copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, acetone, propylene glycol, and mixtures thereof.

It is another object of this invention to provide methods for treating skin or hair using these compositions.

It is another object of this invention to provide methods for styling and holding hair.

These and other objects will become readily apparent from the detailed description which follows.

SUMMARY OF THE INVENTION

The present invention relates to personal care compositions comprising:

(a) an adhesive copolymer having a weight average molecular weight from about 10,000 to about 5,000,000, and
(b) a solvent for said copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, acetone, propylene glycol, and mixtures thereof, wherein said composition, when dried, has a cohesive strength of greater than about 0.5 kgf/mm², a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm³, and an impact strength of greater than about 7000 ergs. The compositions are preferably hair spray compositions having improved removeability, wherein removeability is defined by a hair stiffness value of from 0 to about 3.5 and a hair flaking value of from 0 to 3.5 (0 to 4 scale).

In further embodiments, the present invention relates to a method for treating the skin or hair by applying to the skin or hair an effective amount of a composition comprising,

a copolymer component comprising:

(a) an adhesive copolymer having a weight average molecular weight from about 10,000 to about 5,000,000, and
(b) a solvent for said copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof, wherein said composition, when dried, has a cohesive strength of greater than about 0.5 kgf/mm², a total energy absorption per unit volume of greater than about 0.55 kgf/mm², and an impact strength of greater than about 7000 ergs. These methods are preferably

directed to the hair spray compositions of the present invention having the removeability values (hair stiffness values and hair flaking values) as defined herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an overhead view of a dumbbell-shaped planar dried hair spray film sample useful for measuring the physical properties such as the cohesive strength and total energy absorption per unit volume as described herein.

Fig. 2 illustrates a cross-sectional view, showing the thickness of the dumbbell-shaped dried film illustrated in Fig. 1.

DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are described below. Also included is a nonexclusive description of various optional and preferred components useful in embodiments of the present invention.

The present invention can comprise, consist of, or consist essentially of any of the required or optional ingredients and/or limitations described herein.

All percentages and ratios are calculated on a weight basis unless otherwise indicated. All percentages are calculated based upon the total composition unless otherwise indicated.

All molecular weights are weight average molecular weights and are given in units of grams per mole.

All ingredient levels are in reference to the active level of that ingredient, and are exclusive of solvents, by-products, or other impurities that may be present in commercially available sources, unless otherwise indicated.

All measurements made are at ambient room temperature, which is approximately 73°F, unless otherwise designated.

All documents referred to herein, including all patents, patent applications, and printed publications, are hereby incorporated by reference in their entirety in this disclosure.

The term "suitable for application to human hair" as used herein, means that the compositions or components thereof so described are suitable for use in contact with human hair and the scalp and skin without undue toxicity, incompatibility, instability, allergic response, and the like.

The term kgf is a standard physical term denoting a kilogram of force subjected to gravitational acceleration, i.e. 9.82 m/s².

Adhesive Copolymer

The compositions of the present invention comprise from about 0.1% to about 30%, preferably from about 0.5% to about 20%, and more preferably from about 0.5% to about 10%, by weight of the composition, of an adhesive copolymer.

By "adhesive" is meant that when applied as a solution to a surface and dried, e.g., the hair or skin, the copolymer forms films or welds. Such a film or weld will have adhesive and cohesive strength, as is understood by those skilled in the art.

The copolymers, or salts thereof, of the present invention are soluble or dispersible in a solvent selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof, at a concentration of at least about 0.1 mg/ml, preferably at least about 0.5 mg/ml, and more preferably at least about 1 mg/ml, at about 73°F.

The copolymers of the present invention have a weight average molecular weight, in grams/mole, of at least about 10,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as viscosity, processing, aesthetic characteristics, spreadability, formulation compatibility, etc. The weight average molecular weight is generally less than about 5,000,000, more generally less than about 2,500,000, and typically less than about 1,500,000. Preferably, the weight average molecular weight is from about 10,000 to about 5,000,000, more preferably from about 20,000 to about 1,000,000, even more preferably from about 30,000 to about 500,000, and most preferably from about 50,000 to about 300,000.

A wide variety of adhesive copolymers are useful in the present invention, provided the physical parameters of the dried hair spray film and the solubility or dispersibility requirements and the molecular weight requirements of the copolymer are met.

Adhesive Copolymers

The adhesive copolymers of the present invention are formed from the random copolymerization of vinyl monomer units and macromonomer units containing a polymeric portion and a vinyl moiety copolymerizable with vinyl monomer units. Upon completion of polymerization, the polymeric portion of the macromonomer units can form side chains of the copolymer. The vinyl monomer units and the vinyl moiety portion of the macromonomer units form the backbone. The vinyl monomer and the macromonomer can be selected from a wide variety of structures as long as the copolymer has the required properties described herein.

As will be clear to one skilled in the art, and especially from the Examples, the copolymer may have one or more side chains grafted to the backbone. In addition, the compositions of the present invention can include, in addition to the copolymer, low

levels of the corresponding copolymers having no side chains grafted to the backbone. As known in the art, synthetic graft copolymerization processes may produce a mixture of polymer molecules containing none, one, or more than one side chains covalently bonded to and pendant from the polymeric backbone. From knowledge of the amount and number average molecular weight of side chains in a polymer sample, and the number average molecular weight of the polymer sample, it is possible to calculate the average number of side chains per polymer backbone.

The grafted copolymers should satisfy the following two criteria:

- (2) the polymeric side chain portion is covalently bonded to the backbone portion; and
- (3) the number average molecular weight of the polymeric side chain portion is from about 1000 to about 50,000.

The copolymers of the present invention are prepared by the polymerization combination of vinyl monomers and macromonomers. The copolymers can be synthesized by free radical polymerization of the monomers and macromonomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 3rd edition, John Wiley & Sons, 1991, pp. 198-334. The desired vinyl monomers and macromonomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The copolymer can be further purified, as desired.

As an alternative to a batch reaction, the copolymer can be made by a semi-continuous or continuous process. In the semi-continuous process, two or more additions of monomers or macromonomers are made during the polymerization reaction. This is advantageous when the copolymer is made of several monomers which react during the polymerization at different rates. The proportions of monomers added to the reaction at the separate points of addition can be adjusted by one of ordinary skill in the art such that the polymers of the final product have a more uniform structure. In other

words, the polymers of the final product will have a more consistent monomer content distribution for each of the monomer types charged to the reaction.

Examples of related copolymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. Additional grafted polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al., filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein in their entirety.

The copolymers are prepared by the polymerization combination of vinyl monomers and macromonomers. The copolymer composition is characterized by the amount of each monomer charged to the polymerization reaction vessel, or alternatively used in a continuous or semi-continuous process.

By appropriate selection and combination of the particular vinyl monomer units and macromonomer units, and by the choice of specific relative ratios of the units well within the ability of one of ordinary skill in the art, the copolymers can be optimized for various physical properties and for compatibility with other ingredients commonly used in hair care applications.

Alternatively, the copolymers of the present invention can correspond to block type structures which can be described by the formulas A-B, A-B-A, and -(A-B)_n wherein n is an integer of 2 or greater. A-B represents a diblock structure, A-B-A represents a triblock structure, and -(A-B)_n- represents a multiblock structure. The monomer units used to prepare these block copolymers are as described under the heading below.

Vinyl Monomer Units

The copolymers of the present invention comprise from about 50% to about 98%, preferably from about 60% to about 95%, and more preferably from about 70% to about 90% by weight of the vinyl monomer units. For the block copolymer, the vinyl monomer units can comprise 100%.

The vinyl monomer unit is selected from copolymerizable monomers, preferably ethylenically unsaturated monomers. Either a single type of vinyl monomer unit or combinations of two or more vinyl monomer units can be utilized. The vinyl monomers

are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the vinyl monomer can be reacted with or polymerized with the polysiloxane macromonomers in a polymerization reaction using one or more conventional synthetic techniques, such as ionic, emulsion, dispersion, Ziegler-Natta, free radical, group transfer or step growth polymerization. In the present invention, monomers and macromonomers that are copolymerizable using conventional free radical initiated techniques are preferred. The term "ethylenically unsaturated" is used herein to mean a material that contains at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri- or tetra-substituted.

The monomer units can be derived from hydrophilic monomers (typically polar monomers), or mixtures of such hydrophilic monomers with hydrophobic monomers (typically low polarity monomers), provided that the solubility characteristics of the overall copolymer is achieved. As used herein, "hydrophilic monomers" means monomers which form homopolymers which are substantially water soluble; "hydrophobic monomers" means monomers which form substantially water insoluble homopolymers.

Nonlimiting classes of monomers useful herein include monomers selected from the group consisting of unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated alcohols, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.

Representative examples of such monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl

caprolactam, methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-tri methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octa decanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; dicyclopentenyl acrylate; 4-biphenyl acrylate; pentachlorophenyl acrylate; 3,5-dimethyladamantyl acrylate; 3,5-dimethyladamantyl methacrylate; 4-methoxycarbonylphenyl methacrylate; trimethylsilyl methacrylate; styrene; alkyl substituted styrenes including alpha-methylstyrene and t-butylstyrene; vinyl esters, including vinyl acetate, vinyl neononanoate, vinyl pivalate and vinyl propionate; vinyl chloride; vinylidene chloride; vinyl toluene; alkyl vinyl ethers, including isobutyl vinyl ether and *tert*-butyl vinyl ether; butadiene; cyclohexadiene; bicycloheptadiene; 2,3-dicarboxylmethyl-1,6-hexadiene; ethylene; propylene; indene; norbornylene; β -pinene; α -pinene; salts of acids and amines listed above, and combinations thereof. The quaternized monomers can be quaternized either before or after the copolymerization with other monomers of the graft copolymer.

Preferred monomers include acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and mixtures thereof.

Macromonomer Units

The copolymers of the present invention comprise from about 2% to about 50%, preferably from about 5% to about 40%, and more preferably from about 10% to about 30%, by weight of the copolymer of macromonomer units.

The macromonomer units are copolymerizable with the vinyl monomers, said macromonomers preferably having a vinyl moiety. Either a single type of macromonomer unit or combinations or two or more macromonomer units can be utilized herein. The macromonomers are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the macromonomers can

be reacted with or polymerized with the vinyl monomers in a polymerization reaction using one or more conventional synthetic techniques, as described above.

The macromonomers that are useful herein contain a polymeric portion and a copolymerizable moiety which is preferably an ethylenically unsaturated moiety. Typically, the preferred macromonomers are those that are endcapped with the vinyl moiety. By "endcapped" as used herein is meant that the vinyl moiety is at or near a terminal position of the macromonomer.

The macromonomers can be synthesized utilizing a variety of standard synthetic procedures familiar to the polymer chemist of ordinary skill in the art. Furthermore, these macromonomers can be synthesized starting from commercially available polymers. Typically, the weight average molecular weight of the macromonomer is from about 1000 to about 50,000.

Preferred macromonomers are polyalkylene macromonomers. Polyalkylene macromonomers are exemplified by the general formula:



wherein I is an optionally present initiator (i.e. n = 0 or 1), W is a monomer unit, E is an endcapping group, and m is an integer from about 10 to about 2000.

I is an optionally present chemical initiator moiety. Without being limited by theory, I can be derived from a chemical initiator or solvent used in the synthesis of the macromonomer. Nonlimiting examples of such initiators from which I can be derived include hydrogen ion, hydrogen radical, hydride ion, hydroxide ion, hydroxyl radical, peroxide radical, peroxide anion, C1-C20 carbocations, C1-C20 carbanions, C1-C20 carbon radicals, C1-C20 aliphatic and aromatic alkoxy anions, ammonium ion, and substituted ammonium ions (e.g., C1-C20 alkyl and C1-C20 alkoxy substituted), and mixtures thereof. I can be derived from any useful solvent, nonlimiting examples of which include water, methanol, ethanol, propanol, isopropanol, acetone, hexane, dichloromethane, chloroform, benzene, toluene, and mixtures thereof.

W is selected from one or more monomer units. Nonlimiting classes of such monomers include C1-C18 acrylate esters, C1-C18 methacrylate esters, C2-C30 straight and branched chain alkenes, styrenes, C1-C30 vinyl ethers, C4-C30 straight and branched chain dienes, and mixtures thereof.

Nonlimiting examples of W groups include those selected from the group consisting of t-butyl acrylate, acrylic acid, methacrylic acid, n-propyl methacrylate, iso-butyl acrylate, n-butyl acrylate, dodecyl acrylate, ethyl acrylate, 2-ethylbutyl acrylate, n-heptyl acrylate, n-hexylacrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate,

1-propyl acrylate, 2-ethylhexyl methacrylate, octyl methacrylate, n-dodecyl methacrylate, n-octadecyl methacrylate, n-decyl methacrylate, n-pentyl methacrylate, isobutylene, isoprene, 1,2-butadiene, 1,3-butadiene, 5-methyl-1-hexene, 6-methyl-1-heptene, 4,4-dimethyl-1-pentene, iso-butyl vinyl ether, styrene, 2-methyl styrene, 3-methylstyrene, 4-methyl styrene, 2-t-butyl styrene, 3-t-butyl styrene, 4-t-butyl styrene, and mixtures thereof. A mixture of W units can be used herein. Additionally, these macromonomers can comprise polymers derived from the polymerization of acrylates, methacrylates, and other ethylenic moieties. The polymers derived from these W units can be selected for have either high (>25°C) or low T_g ($\leq 25^{\circ}\text{C}$) values. The term T_g means glass transition temperature, which is familiar to one of ordinary skill in polymer science.

E is a copolymerizable moiety or "endcapping" group. Preferably E is an ethylenically unsaturated moiety. More preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 2-vinylbenzyl, 3-vinylbenzyl, 4-vinylbenzyl, 2-vinylbenzoyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-but enyl, 1-propenyl, isobut enyl, cyclohexenyl, cyclopentenyl, and mixtures thereof. Even more preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-but enyl, 1-propenyl, isobut enyl, and mixtures thereof. Most preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, and mixtures thereof.

Nonlimiting examples of macromonomer units useful herein include those selected from the group consisting of acryloyl, methacryloyl, or 3-, or 4-vinylbenzyl endcapped polymers of poly(n-butyl acrylate), poly(dodecyl acrylate), poly(2-ethylhexyl acrylate), poly(2-ethylbutyl acrylate), poly(n-ethyl acrylate), poly(n-heptyl acrylate), poly(n-hexyl acrylate), poly(iso-butyl acrylate), poly(iso-decyl acrylate, poly(iso-propyl acrylate), poly(3-methylbutyl acrylate), poly(2-methylpentyl acrylate), poly(nonyl acrylate), poly(octyl acrylate), poly(propyl acrylate), poly(2-ethylhexyl methacrylate), poly(tridecyl methacrylate), poly(hexyl methacrylate), poly(decyl methacrylate), poly(octyl methacrylate), poly(octadecyl methacrylate), poly(dodecyl methacrylate), poly(n-pentyl methacrylate), poly(isobutylene), poly(isoprene), hydrogenated poly(1,2-butadiene), hydrogenated poly(1,4-butadiene), hydrogenated poly(isoprene), poly(1,2-butadiene), poly(1-butene), poly(5-methyl-1-hexene), poly(6-methyl-1-heptene), poly(4,4-dimethyl-1-pentene), poly(iso-butyl vinyl ether), poly[4-t-butyl vinyl benzene-co-2-ethylhexyl acrylate], poly[2-ethylhexyl acrylate-co-octyl acrylamide], poly[2-ethyl

vinyl benzene-co-octyl methacrylate)], poly(n-propyl methacrylate-co-methacrylic acid), and mixtures thereof.

Neutralized Copolymers

As is known in the art, polymers which have acidic functionalities, such as carboxyl groups, are usually used in at least partially neutralized form to promote solubility/dispersibility of the polymer. In addition, use of the neutralized form aids in the ability of the dried compositions to be removed from the hair or skin. When neutralized, it is preferred that from about 10% to 100%, more preferably from about 20% to about 90%, and even more preferably from about 40% to about 85%, of the acidic monomers of the copolymer be neutralized.

Any conventionally used base, including organic or inorganic (metallic or other) bases, can be used for neutralization of the polymers. Metallic bases are particularly useful in the present compositions. Hydroxides, where the cation is ammonium, an alkali metal or an alkaline earth metal, are suitable neutralizers for use in the present compositions. Preferred neutralizing agents for use in compositions of the present invention are potassium hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents which may be included in the compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA) and dimethyl stearamine (DMS). Particularly useful neutralizing agents are mixtures of amines and metallic bases.

Polymers having basic functionalities, e.g., amino groups, are preferably at least partially neutralized with an acid, e.g., hydrochloric acid.

Neutralization can be accomplished by techniques well known in the art, and before or after polymerization of the monomers comprising the graft copolymer.

Solubility of the copolymer, as described above, should be determined after neutralization, if any, as well as after addition of other ingredients that may be included in the copolymer/solvent systems.

Preferred Polymers Of The Present Invention

Nonlimiting examples of preferred polymers of the present invention include those selected from the group consisting of poly(t-butylacrylate-co-n-butylacrylate-co-acrylic acid)-graft- poly(t-butylacrylate-co-acrylic acid)-graft-[poly(isobutylene)], poly(4-t-butylstyrene-co-methacrylic acid)-graft-[poly(isobutylene)], poly((t-butylstyrene-co-methacrylic acid)-graft-[poly(2-ethylhexyl methacrylate)]), poly((t-

butylacrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)]-graft[poly(n-propyl methacrylate-co-methacrylic acid)], poly[(t-butylacrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)]-graft-poly(n-propyl methacrylate-co-acrylic acid), poly[(t-butylacrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)]-graft-[poly(styrene-co-methacrylic acid)], and mixtures thereof.

Nonlimiting examples of preferred polymers of the present invention include those selected from the group consisting of poly[(t-butylacrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)]-graft-poly(n-propyl methacrylate-co-methacrylic acid).

More specific examples of copolymers of the present invention include the following, where the composition is given as weight percentage of each monomer used in the polymerization reaction (i.e. the weight percentage of the monomers and macromonomers charged).

poly(t-butylacrylate-co-2-methoxyethylacrylate-co-acrylic acid)-graft-[poly(n-propyl methacrylate-co-methacrylic acid)] having a weight average molecular weight of about 150,000, comprising about 22% t-butylacrylate, 42% 2-methoxyethylacrylate, 18% acrylic acid, 18% poly(n-propylmethacrylate-co-methacrylic acid) macromonomer with a weight average molecular weight of about 6000.

poly[(t-butylacrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-[poly(isobutylene)] having a weight average molecular weight of about 200,000, comprising about 40% t-butylacrylate, 20% n-butylacrylate, 20% acrylic acid, with a molecular weight of about 10,000, and 20% poly(isobutylene) macromonomer with a molecular weight of about 4,000..

Solvent

The compositions of the present invention comprise from about 70% to about 99.9%, preferably from about 75% to about 98%, and more preferably from about 85% to about 98%, by weight of the composition, of a solvent for the copolymer. The solvent is selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50%, by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the

range of from 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the total composition.

In yet another aspect of this invention are provided hair spray compositions which contain reduced levels of volatile organic compounds such as solvents. As used herein, "volatile organic compounds" or "VOCs" are those organic compounds that contain less than 12 carbon atoms or have a vapor pressure greater than about 0.1 mm of mercury. A reduced volatile organic compound hair spray composition of the present invention contains no more than 80% volatile organic compounds.

Properties Of The Dried Copolymer Component

The copolymer component of the personal care compositions of the present invention, when dried, have specific physical properties as defined by the cohesive strength and total energy absorption per unit area. The dried copolymer components also exhibit specific impact strength properties, and when used in the preferred hairspray embodiments of the present invention have an improved removeability as defined in terms of hair stiffness and flaking values.

Cohesive Strength (kgf/mm²)

Cohesion is the strength of the bonds formed within a sample, e.g., a dried hair copolymer solvent composition. The cohesive strength, which is designated as kgf/mm² (kilograms of force per square millimeter) is the maximum unit stress a material will withstand when being subjected to displacement in tension. Stress is the ratio of measured load (kg X f) to the original cross-sectional area (mm²) of the sample.

The cohesive strength of the dried copolymer components of the current invention are determined using the following method. This method is based on ASTM Designation: D 638-91, Standard Test Method for Tensile Properties of Plastics, Published January 1992, herein incorporated by reference in its entirety. The following test method to measure cohesive strength is similar to the ASTM standard, however, several modifications are made to better represent the tensile properties of the dried films. The measurements are made at about 73°F and about 50% relative humidity. The test method, described herein specifically uses a modified dumbbell shape with a thickness equal to about 0.4 mm., and uses an Instron Model Mini-55 (available from Instron Corporation, Canton, MA) as the testing machine for applying the force to the polymer film samples.

A dried film sample is prepared by drying an amount of the hair spray composition (i.e., the silicone-containing adhesive copolymer and solvent selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof, and any

additional optional components) in a flat-bottomed aluminum mold coated with PFA (perfluoroalkoxy) Teflon®. The copolymer film is dried at about 73°F and about 50% relative humidity until film has attained a "constant weight". By "constant weight" is meant that there is less than a 1% weight fluctuation in the sample over a period of 24 hours. The drying film should be kept in an area protected from air currents, which could result in non-uniform drying and formation of air bubbles. The copolymer film is cut into a dumbbell shape for testing. The sample should be substantially free of defects, i.e. cracks, chips, tears, etc. Figures 1 and 2 illustrate the planar dumbbell shaped film to be used in the tensile testing described herein for the cohesive strength and the total energy absorption per unit volume. Figure 1 illustrates an overhead view of the dumbbell shaped sample. Figure 2 illustrates a cross section through the dumbbell shaped sample. The width of the narrow section, 1, of the dumbbell is about 3 mm (1 = 3 mm). The length of the narrow, 3 mm., section of the dumbbell, 3, is about 13 mm. (3 = 13 mm.). The gauge length of the narrow section, 2, is the initial film length used in the determination of the strain of the sample. The gauge length is equal to or less than the length of the narrow section, preferably equal to the length of the narrow section (i.e., 2 = 3). The width of the ends of the dumbbell, 4, are about 10 mm. (4 = 10 mm.). The distance between end sections of the film, 5, is about 28 mm. (5 = 28 mm.). The overall length of the film, 6, is about 64 mm. (6 = 64 mm.). The length of the wide ends of the film is about 18 mm. ((6-5)/2 = 18 mm.). The transition sections between the wide ends and the narrow section of the film are about 6.5 mm. in length (i.e. (5-3)/2 = 6.5 mm.). Also the end portions of the narrow, center portion should be smoothly curved to avoid any stress points in the sample. The curve of the transition section, should have a radius, 7, of from about 0.5 in. to about 5 inches, and should join tangentially to the narrow section. The film is formed to a thickness, 8, of 0.4 mm. (8 = 0.4 mm.). The dumbbell shaped samples are further equilibrated to a "constant weight". By "constant weight" is meant that over a selected 4 day period, there is no more than 0.2% average weight gain or loss, relative to the dumbbell's measured weight 4 days previous and no more than \pm 0.2% weight drift should be observed between two consecutive measurements in the four day period of time. The dumbbell should be tested within a 7 day period of reaching this constant weight.

The samples are tested on a calibrated Instron Model Mini-55 tensile tester. Before mounting the sample into the Instron, the length, 3, width, 1, and thickness, 8, of the narrow section of the dumbbell shaped sample are measured to the nearest micron with a calibrated micrometer. The dimensional measurements are required by the Instron for force per unit area calculations. The wide ends of the dumbbell samples are clamped into

the Instron and pulled at a crosshead rate of 5 mm. per minute. The Instron tester measures the overall forces (e.g., kgf) applied to the film. These forces are spread over the cross sectional area of the narrow section of the film. The cohesive strength of the copolymer is the maximum unit force measured by the Instron divided by the cross sectional area of the narrow portion of the film.

The dried copolymer component of the compositions of the present invention have a cohesive strength of greater than about 0.5 kgf/mm², preferably greater than about 0.6 kgf/mm², and more preferably greater than about 0.7 kgf/mm².

Total Energy Absorption Per Unit Volume (e.g., kgfmm/mm³)

The total energy absorption per unit volume, which is designated as kgfmm/mm³ (kilograms of force millimeters per millimeter cubed), is the ratio of the total energy required to reach the autobreak point (in kgf X mm) to the original volume of the sample (mm³). The total energy required to reach the break point is calculated using standard techniques by determining the area under a load versus displacement curve for the sample. The total energy absorption per unit volume is also known as "toughness" by those skilled in the art of polymer science and materials testing.

The measurements are made at about 73°F and about 50% relative humidity.

The dried copolymer component of the compositions of the present invention have a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm³, preferably greater than about 0.75 kgfmm/mm³, more preferably greater than about 1.10 kgfmm/mm³, more preferably greater than about 1.60 kgfmm/mm³, and most preferably greater than about 2.15 kgfmm/mm³.

Impact Strength

Impact strength is the mean-failure energy (mass X gravity X height) required to produce sample failure, e.g., in a dried hair spray composition. The sample failure is characterized by a crack or split created by the impact of the falling weight that can be seen by the naked eye under normal laboratory lighting conditions.

The impact strength of the dried copolymer components of the compositions of the current invention are determined using the following method. This method is based on ASTM Designation: D 5420-93, Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Striker Impacted by a Falling Weight (Gardner Impact), Published 1995, herein incorporated by reference in its entirety, however, several modifications are made to better represent the impact properties of the dried film. The measurements are made at about 73°F and about 50% relative humidity.

The test method, described herein specifically uses rectangular shaped samples with a thickness equal to about 0.4 mm, and uses a GCA/Precision Scientific Penetrometer modified to drop a blunt faced probe to a distance of 70 mm and equipped with a Precision Scientific solenoid controller for GCA Penetrometer, a blunt faced cylindrical probe with a surface area of 8 mm² (OK M&T Corp. - part# WSU30), and a ruler which measures in 1 mm increments.

The samples are prepared using the film drying method described above in the cohesive strength measurements. The copolymer film is cut into the rectangular shape, e.g. 10 mm X 20 mm. The thickness of the sample is 0.4 mm. The film thickness of various test samples should be maintained within $\pm 15\%$ of 0.4 mm.

The following measurement process is used. Turn on the solenoid operated probe release controller. The controller should begin to cycle on and off as indicated by a red light. Be sure the probe face is flush with the impact surface so that the sharp edge of the probe does not strike the film. Place a film sample on the Impact Tester over the target area. Direct the metric ruler gently on the film sample. Direct the lightening source across the surface of the sample such that the light source is in the same plane as the surface of the film. Small fractures in the film will reflect light and be easily detected. Move the probe up to desired drop distance. A suggested distance progression is: 1 mm, 3 mm, 5 mm, 10 mm, 15 mm, 20 mm, 25 mm, and further 5 mm increments up to 70 mm. (70 mm is the upper limit of the instrument). Turn on the instrument switch, to drop the probe onto the sample. The first step in the measurement of impact energy is to find the range of probe height necessary to fracture the film. Start at 1 mm for the first step. Continue to move up according to the suggested distance progression until a fracture is observed. When a fracture is observed make a note of it and move to a new sample. The second step in determining impact energy is to set a new sample and start drop at an observed fracture point in the range procedure. Set a new film sample and move the probe to the next lowest setting. If the film fractures, record result and repeat previous step. If the film does not fracture, set a new sample and move to the next distance. Continue to set new samples and increase the drop distance until the film fractures. Continue the procedure until 5 fractures are observed. Calculate the amount of work energy, i.e. the fracture strength using the following formula:

$$W = m \times g \times h, \text{ where}$$

W = amount of work energy in ergs,

m = mass of probe (59.53 g) (The probe is removable and can be replaced with one of different mass or impact surface area).

g = gravitational constant (980.665 cm/sec²),

h = average distance probe travels to impact (cm).

The dried hair spray compositions of the present invention have an impact strength of greater than about 7000 ergs, preferably greater than about 20,000 ergs, and more preferably greater than about 50,000 ergs.

Hair Spray Removeability

The adhesive copolymers herein have improved removeability when used in the preferred hairspray embodiments of the present invention. In this context, removeability means that the adhesive copolymers are more easily removed from the hair or other applied surface during shampooing.

For purposes of defining the preferred hair spray compositions of the present invention, removeability is determined indirectly by evaluating hair stiffness and the appearance of observable white flakes after treating the hair in accordance with the removeability methodology described hereinafter. It has been found that the removeability of a hair spray formulation after shampooing correlates with the resulting stiffness/softness of the hair and the appearance/nonappearance of white flakes on the hair after a series of shampooing cycles. The hair spray compositions of the present invention have high removeability e.g., reduced stiffness and reduced white flaking. The term "removeability" as used herein therefore refers to hair stiffness values (0-4 scale) and white flaking values (0-4 scale) as measured in accordance with the methodology described hereinafter.

For purposes of defining the preferred hair spray compositions of the present invention, the removeability of the hair spray compositions is defined as a combination of hair stiffness values and hair flaking values, wherein the hair spray compositions provide hair flaking values ranging from 0 to about 3.5, preferably from 0 to about 2.5, more preferably from 0 to about 2.0, and hair stiffness values ranging from 0 to about 3.5, preferably from 0 to about 2.5, more preferably from 0 to about 2.0.

Methodology: Hairspray Removeability

Removeability of the hairspray composition of the present invention, as indirectly evaluated in terms of hair stiffness and the appearance of white flakes, is determined in accordance with the following methodology. The methodology simulates multiple application and multi-cycle application of hairspray compositions so as to indirectly determine how readily and effectively such hairspray compositions are removed from hair.

The methodology described herein provides a means of evaluating hair switches blindly treated with hairspray embodiments of the present invention. The method by which each hair switch is treated with the hairspray embodiments, and the method by which each treated hair switch is then evaluated for removeability are described in detail below.

Two trained panelists each evaluate identically treated hair switches or sets of hair switches for stiffness and the appearance of white flakes. The panelists then individually assign each of the treated hair switches with a numerical score (0 to 4 scale) for hair stiffness and a numerical score for flaking (0 to 4 scale). The order in which the hair switches are treated with different hair spray embodiments is randomized and conducted round robin. Two identical sets of switches are prepared as described below for each panelist so that each has a fresh set of switches to evaluate. Before evaluating the blindly treated hair switches, each panelist also evaluates (not blinded) an untreated hair switch as a zero reference for hair stiffness and flaking. Each panelist also evaluates a control treated hair switch as a flaking reference (score 4.0) and another control treated hair switch as a hair stiffness reference (score 4.0). The hair stiffness values as defined herein are determined by averaging the hair stiffness scores provided by the two panelist. Likewise, the hair flaking values as defined herein are determined by averaging the hair flaking scores provided by the two panelists.

The hair switches are treated with either an aerosol or non-aerosol hair spray embodiment of the present invention in accordance with the following steps. The hair stiffness reference and the flaking reference are also prepared in accordance with the following steps, except that each is treated with the corresponding hair spray formulations as described hereinafter in Tables 2 and 3.

- 1) Vertically suspend a clean hair switch (10 inch European virgin brown hair, 20 gram) from its bound end and comb (black rubber comb, 5 inches by 1 inch, 1/2 fine tooth) through the switch to remove any tangles.
- 2) If necessary, use a static gun to eliminate any static build-up on the switch.
- 3) For non-aerosol products, spray the switch from a distance of 4 inches while applying ten pumps of the product to the switch and while moving the atomized spray pattern in a fluid up-and-down motion to cover the entire switch, or for aerosol products, spray each switch from a distance of 6 inches while applying the aerosol stream to the switch for a period of 3 seconds and while moving the aerosol stream in a fluid up-and-down motion to cover the entire switch.
- 4) Repeat step 3 on the opposite side of the switch.

- 5) After spraying the opposite side of the switch, hang the treated switch from its bound end to allow it to dry for one hour at ambient temperature, pressure and humidity.
- 6) Comb the dried switch using a black rubber comb (5 inches x 1 inch, 1/2 inch fine tooth) by combing away from the bound end of the switch but by initially starting toward the unbound end taking smaller strokes and then gradually taking larger strokes until the comb passes through the entire unbound length of the treated switch.
- 7) Repeat steps 1 through 6.
- 8) Wet the treated hair switch with water (+15-20 grain hardness, 38°C, 1 gal/min. water pressure).
- 9) Apply 1 ml of shampoo (Table 1: methodology shampoo) along the length of the front of the wet hair switch and apply another 1 ml of the shampoo along the length of the reverse side of the wet hair switch.
- 10) Gently milk the switch from top to bottom (hand over hand between thumb and fingers) for 15 seconds at 1 stroke per second.
- 11) Rinse the hair switch with water (38°C, +15-20 grain hardness, 1 gal/min. water pressure) for 15 seconds. Gently squeeze the hair between the first and second fingers, drawing the fingers down the switch after 5 seconds, 10 seconds, and after final rinse.
- 12) Hang the treated switch and allow it to dry for two hours at 60°C in a hot box.
- 13) Remove the dried switches from the hot box.
- 14) Comb the dried switch using a black rubber comb (5 inches x 1 inch, 1/2 inch fine tooth) by combing away from the bound end of the switch but by initially starting toward the unbound end taking smaller strokes and then gradually taking larger strokes until the comb passes through the entire unbound length of the treated switch.
- 15) Repeat steps 1-14.
- 16) Repeat steps 1-13.
- 17) A panelist then evaluates the treated switch by feeling it between their first and second fingers of their dominant hand and between their thumb and other fingers for stiffness and resistance to bending, and then assigns to the treated switch a hair stiffness score (0 to 4 scale). The value of the assigned score is relative to the hair stiffness reference score (4) and the untreated reference score (0).
- 18) The panelist then combs the evaluated switch in accordance with the procedure set forth in Step 14 above, and then visually evaluates the combed switch for

white flakes, coating, and white haze and assings it a hair flaking score (0 to 4 scale). The value of the assigned score is relative to the hair flaking reference score (4) and the untreated reference score (0).

Table 1: Methodology Shampoo

Ingredient List	Percent Composition As Added	Percent Composition Chemical Content
Sodium Laureth Sulfate	40.0000	10.0000
Water - USP Purified	30.3000	30.3000
Sodium Lauryl Sulfate	29.1000	8.0025
Cocamide DEA	.5000	.4000
Kathon CG	.1000	.0015
Citric Acid Solution (50% active)	** adj. from 0 - 1% (note: water level qs. to 100%)	

Table 2: High Flaking Control

Raw Materials	Percent Composition As Added	Percent Composition Chemical Content
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (National Starch lot AF-6713)	4.50	4.50
Water - USP Purified	15.50	15.50
Ethanol (SDA 40)	80.00	80.00

Table 3: High Stiffness Control

Raw Materials	Percent Composition As Added	Percent Composition Chemical Content
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (National Starch lot AF-6713)	6.00	6.00
Aminomethylpropanol, 95%	1.04	0.99
Water - USP Purified	15.50	15.50
Diisobutyl Adipate	0.20	0.20

Ethanol (SDA 40)	80.00	80.00
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Each of the formulations described in Tables 1-3 are prepared by conventional formulation and mixing techniques.

Optional Ingredients

The compositions of the present invention can also comprise a wide variety of optional ingredients that are suitable for application to human hair.

The compositions hereof can optionally contain a plasticizer for the copolymer. Any plasticizer suitable for use in hair care products or for topical application to the skin or hair can be used. A wide variety of plasticizers are known in the art. These include glycerin, diisobutyl adipate, butyl stearate, propylene glycol, tri-C₂-C₈ alkyl citrates, including triethyl citrate and tri-propyl, -butyl, -pentyl, etc., analogs of triethyl citrate. Triethyl citrate is preferred.

Plasticizers are typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%. Preferably, the weight ratio of graft copolymer to the plasticizer is from about 1:1 to about 40:1, preferably from about 2:1 to about 30:1, more preferably from about 3:1 to about 25:1.

Optionally, the compositions of the present invention can contain an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the hair spray composition. When used, the ionic strength modifiers will be present in the present compositions at a level of at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the hydrophilic liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH⁻ and H⁺ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and triethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling

composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The use of ionic strength modifiers are especially useful in reduced volatile organic solvent compositions.

The present compositions can also contain various hydrophobic volatile solvents such as cyclomethicone and volatile hydrocarbons such as isododecane and isoheptadecane.

The present compositions can contain a wide variety of other optional ingredients, including among them any of the types of ingredients known in the art for use in hair care compositions, especially hair setting compositions such as especially hair spray compositions and hair setting tonics. Generally, such other adjuvants collectively can comprise from about 0.05% to about 5% by weight and preferably from about 0.1% to about 3%, by weight. Such conventional optional adjuvants are well known to those skilled in the art and include, but are not limited to, surfactants (which may be anionic, cationic, amphoteric, or zwitterionic and which include fluorinated surfactants and silicone copolyols), propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.); emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents; sunscreens; preservatives; thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

Personal Care Products

The compositions of the present invention can be formulated as a wide variety of personal care products. Such products can include shampoos, soaps, hairsprays, lotions, creams, antiperspirants, anti-acne products, nail enamels, lipsticks, foundations, mascaras, and sunscreens.

In preferred embodiments, the compositions of the present invention are formulated as hair spray compositions. These hairspray compositions preferably have removable values as defined hereinbefore, and may be dispensed as sprayed or atomized products from containers which are pump spray dispensers or aerosol canisters. Such containers are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants can be used to propel the compositions. A suitable propellant for use can be generally any liquifiable gas conventionally used for aerosol containers. Suitable propellants for use are volatile hydrocarbon propellants which can include liquified lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, nitrogen, carbon dioxide, nitrous oxide, and atmospheric gas. The hydrocarbons, particularly isobutane, used singly or admixed with other hydrocarbons are preferred.

The aerosol propellant may be mixed with the present hair spray compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 50% by weight of the total composition.

Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the trademark SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their trademark VIDAL SASSOON AIRSPRAY® hair sprays.

Conventional nonaerosol pump spray dispensers, i.e., atomizers, can also be used.

Other hair styling compositions include tonics and lotions, which are typically dispensed in a conventional bottle or tube, and applied directly to the hair or first dispensed to the hand and then to the hair.

Method of Making

The compositions of the present invention, including the preferred hairspray embodiments, can be made using conventional formulation and mixing techniques. The adhesive copolymer and the solvent are mixed to provide a homogeneous mixture. Any

other ingredients are then added and mixed to yield the final composition. If the polymer is neutralized, the neutralizer is preferably added prior to addition of other ingredients. For hair spray products, the composition is packaged in conventional mechanical pump spray devices, or alternatively, in the case of aerosol sprays products, the composition is packaged in conventional aerosol canisters along with an appropriate propellant system.

Method of Use

The compositions of the present invention, including the preferred hairspray embodiments of the present invention, are used in conventional ways to provide the benefits of the present invention. These products can be applied to the skin or hair. Typical amounts of products can range from about 0.1 mg/cm² to about 25 mg/cm² of skin or hair, although a wider range can be used depending upon the exact product application. For hair care products, the methods generally involve application of an effective amount of the product to dry, slightly damp, or wet hair before and/or after the hair is dried and arranged to a desired style. Application of the product is normally effected by spraying or atomizing the product using an appropriate device, e.g. a mechanical pump spray, a pressurized aerosol container, or other appropriate means. The composition is then dried or allowed to dry. By "effective amount" is meant an amount sufficient to provide the hair hold and style benefits desired. In general, from about 0.5g to about 30g of product is applied to the hair, depending upon the particular product formulation, dispenser type, length of hair, and type of hair style.

The following Experiments and Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

Examples

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name.

Examples 1-4: Syntheses of macromonomers and copolymers.

Example 1

Synthesis of Vinylphenyl-terminated Poly(n-Propyl methacrylate-co-Methacrylic Acid) Macromonomer

Into a round-bottomed-flask fitted with magnetic stirring and under slight argon pressure (8 psi), is added tetrahydrofuran (1L), trimethylsilylmethacrylate (100g, 0.632 mole), and n-propylmethacrylate (100g, 0.780 mole). The solution is cooled to -80C then initiated with diphenylhexylolithium (0.0275 moles) for chain propagation via anionic polymerization mechanism. After continuous stirring for 0.5 h, vinylbenzoyl chloride (8.33 mL, 0.05 mole) is charged to the solution and continued stirring for 0.5 h. The solution is then warmed to ambient temperature and H₂O (10mL) is added and stirred for 0.25 hours to deprotect the acid groups. The macromonomer, which has a weight average molecular weight of about 6000, is obtained by precipitating the resulting solution in hexanes, collecting precipitate, and drying under vacuum.

Example 2

Synthesis of Poly(t-butylacrylate-co-2-methoxyethylacrylate-co-acrylic acid)-graft-[poly(Propyl methacrylate-co-Methacrylic Acid)] Copolymer

To a round-bottomed-flask equipped with a reflux condenser, temperature control, mechanical stirring mechanism, and under slight argon pressure (8psi), is added acetone (0.5L), t-butylacrylate (24g), 2-methoxyethylacrylate (38g), acrylic acid (19g), and vinylphenyl-terminated (n-propylmethacrylate-co-methacrylic acid) macromonomer (19g) (from Example 1). Solution is stirred until all components are dissolved, then heated to 60C. Azobisisobutyronitrile (0.7g) is charged to the system. After 10h, solution is cooled and precipitated in water to yield silicone modified graft copolymer.

Example 3

Synthesis of Acryloyl Encapped Polyisobutylene Macromonomer

Prepare a solution of 100 grams (0.024 mol) hydroxyl endcapped polyisobutylene polymer (PIB-OH) having a weight average molecular weight of 4,172 g/mol by conventional living carbocationic polymerization of isobutylene (for example, as described in G. Kaszas, Poly. Bull., 20, 413 (1989). Add a two fold mole excess (4.84 g, 0.048 mol) triethylamine to the solution. Add this solution dropwise to a solution of acryloyl chloride (4.35 g, 0.048 mol) in dry methylene chloride (100 g) at 0 °C. Stir for about 12 hours at room temperature, filter the mixture and evaporate the excess triethylamine and methylene chloride to obtain acryloyl endcapped polyisobutylene macromonomer.

Example 4Synthesis of Poly[(t-butylacrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-[poly(isobutylene)]]

Place 22 parts acrylic acid, 44 parts t-butyl acrylate, 22 parts n-butylacrylate, 12 parts polyisobutylene macromonomer (4172 MW) (from Example 5) in a flask. Add sufficient tetrahydrofuran as the reaction solvent to produce a final monomer concentration of about 20%. Purge the vessel with an inert atmosphere, preferably nitrogen or argon. Add initiator, (2,2'-azobisisobutyronitrile) to a level appropriate for the desired molecular weight. Typically this is in the range of 0.5% to 1.0% by weight relative to the amount of monomer. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature. The polymer is purified by drying off the reaction solvent in an oven. Alternatively, acetone can be used in place of tetrahydrofuran, in which case the polymer is precipitated by adding water and the precipitated polymer is collected and dried.

Examples 5-12

The following examples represent nonaerosol hairspray compositions of the present invention.

Component (wt%)	Example No.							
	5	6	7	8	9	10	11	12
Copolymer 4	4.00	5.00	6.00	4.00	—	—	—	—
Copolymer 2	—	—	—	—	3.00	3.50	2.50	4.00
Isododecane ¹	1.00	—	—	—	—	1.0	2.0	—
Diisobutyl adipate	0.40	—	0.90	0.55	—	—	—	0.40
Sodium hydroxide ²	0.96	1.20	1.44	—	—	1.20	—	1.35
Potassium hydroxide ³	—	—	—	1.21	1.00	—	0.70	—
Perfume	0.10	0.10	0.10	0.10	0.10	0.15	0.10	0.15
Water	QS10	QS10	QS10	QS10	QS10	QS10	QS10	QS10
	0	0	0	0	0	0	0	0
Sodium Benzoate	—	—	—	—	0.10	0.10	—	0.10
Ethanol ⁴	76.54	71.95	81.56	71.25	79.40	69.26	78.00	55.00

1 PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

2 Sodium hydroxide is 30% active.

3 Potassium hydroxide is 45% active.

⁴ SDA 40 (100% ethanol).

Examples 13-18

The following examples represent aerosol hairspray compositions of the present invention.

Component (wt%)	13	14	15	16	17	18	<u>Example No.</u>
Copolymer 2	5.00	4.00	3.50	—	—	—	
Copolymer 4	—	—	—	4.00	3.00	4.00	
Isododecane ¹	0.50	—	—	—	—	0.50	
Triethyl citrate ²	—	—	0.21	—	—	—	
Diisobutyl adipate	0.70	0.45	—	0.40	0.25	0.35	
Propylene glycol	—	—	0.30	—	—	—	
Sodium hydroxide ³	1.00	—	—	—	1.0	—	
Potassium hydroxide ⁴	—	0.94	1.20	1.04	—	1.20	
Perfume	0.10	0.10	0.10	0.10	0.10	0.10	
Water	QS100	QS100	QS100	QS100	QS100	QS100	
Sodium Benzoate	0.10	0.10	—	0.10	0.20	—	
Ethanol ⁵	56.69	57.42	72.0	50.0	30.00	54.5	
Propellant - Isobutane	—	—	7.02	15.00	10.00	—	
Propellant - n-butane	10.00	—	—	—	—	—	
Propellant -	10.00	—	—	15.00	15.00	—	
Dimethyl ether ⁶	—	—	—	—	—	—	
Propellant -	—	25	15.98	—	—	32.32	
Hydrofluorocarbon 152a ⁷	—	—	—	—	—	—	

¹ PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

² CITROFLEX-2, from Morflex, Inc., Greensboro, NC, USA.

³ Sodium hydroxide is 30% active.

⁴ Potassium hydroxide is 45% active.

⁵ SDA 40 (100% ethanol).

⁶ DYMEL - A, from Dupont.

⁷ DYMEL-152a, from Dupont.

The compositions are prepared as described above, by first mixing the polymer with the ethanol, neutralizing the polymer with sodium or potassium hydroxide, then

adding sequentially (as applicable) with mixing, isododecane, plasticizer, perfume, and water. If sodium benzoate is used, it is added after water addition. Most preferably a premix of water and sodium benzoate is made and then added after the main water addition. Propellants for aerosol compositions are charged to conventional aerosol containers after the remainder of the prepared composition has been added.

The hair spray embodiments of the present invention described in Examples 5-18 have high removeability from hair, and when evaluated by the removeability methodology described herein, provide a hair stiffness value of less than 2.0 and a hair flaking value of less than 2.0.

While particular embodiments of the subject invention have been described, it will be obvious to those skilled in the art that various changes and modifications to the subject invention can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of the subject invention.

EXAMPLE 19

The following is a hair conditioner composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	Q.S. to 100%
Perfume	0.10
Stearalkonium Chloride	0.87
Methylchloroisothiazolinone	0.03
Methylisothiazolinone	0.03
Sodium Hydroxide Solution (30% by weight)	0.70
Polymer 2	3.00
Ethanol	20.0

This product is prepared by dispersing the copolymer 3 in ethanol then adding the remaining ingredients and stirring for about 30 minutes.

EXAMPLE 20

The following is a hair styling gel composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer 4	2.50

Water	QS 100%
Carbomer 940	0.50
Sodium Hydroxide Solution (30% by weight)	0.80
Panthenol	0.05
Polysorbate 80	0.20
Perfume	0.20

This product is prepared by dispersing the copolymer # 4 and carbomer 940 in water and adding the sodium hydroxide. The mixture is stirred for approximately one half hour and the remaining components are added.

EXAMPLE 21

The following is a spray-on gel hair composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	Q.S. to 100 %
Ethanol	15.00
Panthenol	0.05
Potassium Hydroxide Solution (45% by weight)	0.50
Perfume	0.20
Copolymer # 2	2.00

This product is prepared by dissolving the copolymer # 2 ethanol and then adding the water and potassium hydroxide solution to facilitate the incorporation of the copolymer into the solvent. The mixture is stirred for one half hour and the other components are mixed in.

EXAMPLE 22

The following is a hair styling mousse composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	Q.S. to 100 %
Lauramine Oxide	0.20
Panthenol	0.05
Perfume	0.05
Copolymer #4	3.00
Sodium Hydroxide Solution (30% by weight)	1.00
Isobutane	7.00

This product is prepared by dissolving the copolymer #2 in water and adding the sodium hydroxide solution with mixing for one half hour. The other components (except isobutane) are added and mixed for an additional 10 minutes. Aluminum aerosol cans are then filled with 93 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 7 parts Isobutane. This composition is useful for application to the hair to provide conditioning, styling and hold.

EXAMPLE 23

Sunscreen Composition

<u>Ingredients</u>	<u>Weight %</u>
Water	QS100
Carbomer 1342 ^[1]	0.16
Octyl Methoxycinnamate	0.50
Dimethicone copolyol	0.10
Tocopheryl Acetate	0.10
Sodium Hydroxide (30% sol. by weight)	1.50
Ethanol	40.00
Copolymer #4	4.00

[1] Available as Carbopol® 1342 from B.F. Goodrich.

The water, ethanol, sodium hydroxide solution and polymer 4 are mixed for one half hour. The remaining ingredients are added and mixed for an additional half hour.

EXAMPLE 24

The following is an anti-acne composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer # 2	2.00
Water	Q.S. to 100 %
Ethanol (SDA 40)	40.00
Carbomer 940	0.75
Sodium Hydroxide Solution (30% by weight)	0.90
Salicylic Acid	2.00

This product is prepared by mixing the water, ethanol, copolymer 2, and carbomer together for about 10 minutes. The remaining ingredients are added and the mixture is stirred for an additional 30 minutes. This composition is useful for application to the skin to provide improved water resistance and is useful in the treatment of acne.

EXAMPLE 25

The following is a nail polish clear coat composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer # 4	15.00
Ethanol	42.00
Acetone	40.00
NaOH soln., 30%	3.00

This product is prepared by mixing all the ingredients until dispersed.

EXAMPLE 26

The following is a facial wrinkle remover composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer # 4	6.00
NaOH soln., 30%	2.10
DRO water	q.s.

This product is prepared by mixing all the ingredients until dispersed.

EXAMPLE 27

The following is a styling lotion composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer # 2	4.00
Natrosol 250HH ¹	0.50
NaOH soln., 30%	1.35
Kathon CG	0.03
Ethanol	8.00
DRO water	q.s.

¹ Natrosol 250HH-Hydroxyethylcellulose offered by Aqualon.

The copolymer is first dissolved in the ethanol and then added to a premix composed of the remaining ingredients and mixed until well dispersed.

EXAMPLE 28

The following is an aftershave splash composition representative of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Copolymer # 2	2.00
NaOH soln., 30%	0.60
Ethanol	50.00
Perfume	0.20
Menthol	0.20
DRO water	q.s.

This product is prepared by mixing all the ingredients until dispersed.

What is claimed is:

1. A personal care composition, comprising:
 - (a) an adhesive copolymer having a weight average molecular weight from 10,000 to 5,000,000, and
 - (b) a solvent for said copolymer selected from the group consisting of water, ethanol, n-propanol, isopropanol, acetone, propylene glycol, and mixtures thereof,wherein said composition, when dried, has a cohesive strength of greater than 0.5 kgf/mm², a total energy absorption per unit volume of greater than 0.55 kgfmm/mm³, and an impact strength of greater than 7000 ergs.
2. A composition according to Claim 1 wherein the composition is a hair spray composition which provides a hair stiffness value of from 0 to 2.0 and a hair flaking value of from 0 to 2.0.
3. A composition according to either of Claims 1 or 2 wherein said copolymer is soluble or dispersible in said solvent at a concentration of at least 0.1 mg/mL at 73°F.
4. A composition according to any one of the preceding claims wherein said composition, when dried, has a cohesive strength of greater than 0.7 kgf/mm², a total energy absorption of greater than 1.10 kgfmm/mm³, and an impact strength of greater than 50,000 ergs.
5. A composition according to any one of the preceding claims wherein said copolymer is formed from the random copolymerization of the following relative weight percentages of vinyl monomer units and polysiloxane-containing macromonomer units:
 - a. from 50% to 98%, by weight of said copolymer, of vinyl monomer units, and
 - b. from 2% to 50%, by weight of said copolymer, of macromonomer units, wherein said polysiloxane-containing macromonomer units have a weight average molecular weight from 1,000 to 50,000.
6. A composition according to Claim 5 wherein said vinyl monomer units are selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride, vinyl toluene, butadiene, cyclohexadiene, ethylene, propylene n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and combinations thereof.

7. A composition according to any one of preceding Claims 1, 2, 3 or 4 wherein said copolymer is a block copolymer.
8. A composition according to any one of preceding Claims 1, 2, 3 or 4 wherein said copolymer is a graft copolymer.
9. A method of styling hair comprising the step of applying to the hair an effective amount of a composition according to any one of the preceding claims.

1/1

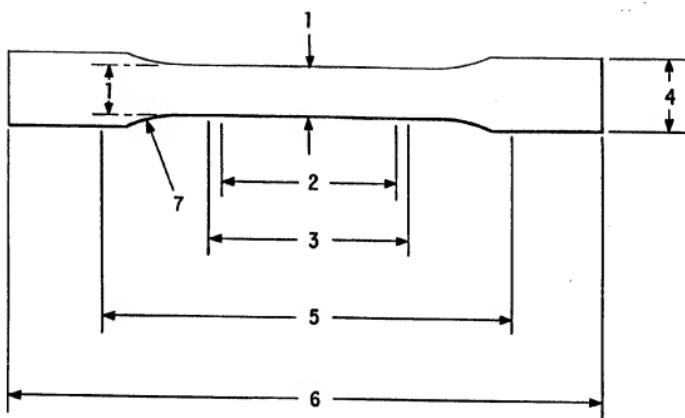


FIG. 1

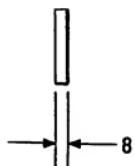


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/08347A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 766 957 A (WAKO PURE CHEM IND LTD ;MANDOM CORP (JP)) 9 April 1997 see abstract; examples -----	1,2,5-7, 9
T	US 5 653 968 A (CARBALLADA JOSE ANTONIO ET AL) 5 August 1997 see column 2, line 12 - line 49 see column 4, line 44 - column 5, line 28 see column 7, line 18 - line 67 -----	1,2,5,6, 8,9
A	WO 96 32918 A (PROCTER & GAMBLE) 24 October 1996 -----	
A	EP 0 408 311 A (MITSUBISHI PETROCHEMICAL CO) 16 January 1991 cited in the application -----	

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

Date of mailing of the international search report

7 August 1998

17/08/1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/08347

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<p>(54) Title: PERSONAL CARE COMPOSITIONS CONTAINING LINEAR TOUGHENED SILICONE GRAFTED POLYMERS</p> <p>(57) Abstract</p> <p>A personal care composition comprising: (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises: (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120 °C to about 25 °C and (ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25 °C to about 250 °C wherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and (b) a personal care carrier.</p>			

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PERSONAL CARE COMPOSITIONS CONTAINING LINEAR TOUGHENED SILICONE GRAFTED POLYMERS

TECHNICAL FIELD

The present invention relates to personal care compositions, such as haircare, cosmetic and nail compositions containing linear toughened silicone grafted polymers.

BACKGROUND OF THE INVENTION

Cosmetic compositions such as lotions, creams, emulsions, packs, make-up (e.g., foundations, lipsticks, eye shadows and the like) and hair compositions are used to improve one's outward appearance. Many personal care products use contain various resins, gums, and adhesive polymers. The polymers are used for a variety of purposes including thickening, feel properties, film-forming ability, active deposition, active penetration, hair holding, etc. Consequently there is constantly a search for developing polymers having improved properties for use in personal care product. Many of these compositions require the use of adhesive silicone grafted polymers. For example, the desire to have the hair retain a particular shape is widely held. The most common methodology for accomplishing this is the application of a styling composition to dampened hair, after shampooing and/or conditioning, or to dry, styled hair. These compositions provide temporary setting benefits and they can be removed by water or by shampooing. The materials used in the compositions to provide the setting benefits have generally been resins and have been applied in the form of mousse, gels, lotions or sprays.

Many people desire a high level of style retention, or hold, from a hair spray composition. In typical hair sprays, hold is achieved by the use of resins, such as AMPHOMERR^R, supplied by National Starch and Chemical Company, and GANTREZ^R SP 225, supplied by GAF. In general, as hair hold for hair spray compositions is increased, the tactile

feel of the hair becomes stiffer and hence, less desirable. It is desirable to provide hair spray products which could provide an improved combination of hair hold and hair feel characteristics.

Recently, it has become known to utilize silicone grafted organic backbone polymers in various personal care compositions including their use as hair setting agents in hairspray compositions and other hair styling compositions, e.g. hair tonics, lotions, rinses, mousses, etc. Silicone grafted polymers can be used to make personal care compositions with improved feel, e.g., in the case of hair sprays, increased softness relative to conventional polymeric hair setting agents.

However, it remains desirable to improve the performance of these silicone grafted polymers. It is an object of this invention to provide personal care compositions containing linear toughened silicone graft copolymers.

It is a further object of this invention to provide personal care compositions containing resins that have improved adhesive and cohesive properties thereby providing improved durability benefits (e.g., style benefits).

These and other benefits as may be apparent from the description below can be obtained by the present invention.

The present compositions can comprise, consist of, or consist essentially of any of the required or optional ingredients and/or limitations described herein.

All percentages and ratios are calculated on a weight basis unless otherwise indicated. All percentages are calculated based upon the total composition unless otherwise indicated.

All ingredient levels refer to the active level of that ingredient, and are exclusive of solvents, by-products, or other impurities that may be present in commercially available sources, unless otherwise indicated.

SUMMARY OF THE INVENTION

The present invention relates to a personal care composition comprising:

- (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises
 - (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and
 - (ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° Cwherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and
- (b) a personal care carrier.

DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are described below. Also included is a nonexclusive description of various optional and preferred components useful in embodiments of the present invention.

Silicone Grafted Adhesive Polymer

The compositions according to the invention comprise, as an essential component, a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises:

- (a) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and

(b) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° C

wherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number-average molecular weight of said silicone macromers is greater than about 1000. This silicone containing hair styling polymer is preferably colloidally dispersed or solubilized in any applicable carrier.

The compositions hereof will generally comprise from about 0.1% to about 99%, preferably from 0.5% to about 50%, more preferably from about 1% to about 10%, by weight of the composition, of the silicone grafted polymer. It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive or film-forming properties to the composition and the composition can be formulated and effectively applied for its intended purpose. By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film or a weld. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

The silicone grafted polymers are characterized by polysiloxane moieties covalently bonded to and pendant from a polymeric carbon-based backbone.

The backbone will preferably be a carbon chain derived from polymerization of ethylenically unsaturated monomers. The backbone comprises (a) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and (b) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° C. The polysiloxane moieties can be substituted on the polymer or can be made by co-polymerization of polysiloxane-containing polymerizable monomers (e.g. ethylenically unsaturated monomers, ethers,

and/or epoxides) with non-polysiloxane-containing polymerizable monomers.

The polysiloxane-grafted polymer should have a weight average molecular weight of at least about 20,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000.

Preferably, the adhesive hereof when dried to form a film have a Tg of at least about -20°C, more preferably at least about -5°C, so that they are not unduly sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the backbone of the polymer, if such a transition exists for a given polymer. Preferably, the Tg is above about -20°C, more preferably above about -5°C. Preferably the adhesive polymer of the present invention has a Tg below about 60°C, more preferably below about 50°C and most preferably below about 40°C.

The silicone grafted polymers for the compositions of the present invention comprise "silicone-containing" (or "polysiloxane-containing") monomers, which form the silicone macromer pendant from the backbone, and non-silicone-containing monomers, which form the organic backbone of the polymer.

When used in a composition, such as a personal care composition for application to the hair or skin, the non-polysiloxane portion should permit the polymer to deposit on the intended surface, such as hair or skin.

The polysiloxane macromer should have a weight average molecular weight of at least about 1000, preferably from about 1,000 to about 50,000, more preferably from about 5,000 to about 50,000, most preferably about

8,000 to about 25,000. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers, including vinyl monomers, and other condensation monomers (e.g., those that polymerize to form polyamides and polyesters), ring-opening monomers (e.g., ethyl oxazoline and caprolactone), etc.

The preferred silicone grafted polymers are comprised of monomer units derived from: at least one free radically polymerizable ethylenically unsaturated monomer or monomers and at least one free radically polymerizable polysiloxane-containing ethylenically unsaturated monomer or monomers.

Vinyl Monomer Units

The silicone copolymers of the present invention comprise from about 50% to about 98%, preferably from about 60% to about 95%, and more preferably from about 70% to about 90% by weight of the vinyl monomer units.

The vinyl monomer unit is selected from copolymerizable monomers, preferably ethylenically unsaturated monomers. The vinyl monomers are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the vinyl monomer can be reacted with or polymerized with the polysiloxane macromonomers in a polymerization reaction using one or more conventional synthetic techniques, such as ionic, emulsion, dispersion, Ziegler-Natta, free radical, group transfer or step growth polymerization. In the present invention, monomers and macromonomers that are copolymerizable using conventional free radical initiated techniques are preferred. The term "ethylenically unsaturated" is used herein to mean a material that contains at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri- or tetra-substituted.

The monomer units can be derived from hydrophilic monomers (typically polar monomers), or mixtures of such hydrophilic monomers with hydrophobic monomers (typically low polarity monomers), provided that the

solubility characteristics of the overall copolymer is achieved. As used herein, "hydrophilic monomers" means monomers which form homopolymers which are substantially water soluble; "hydrophobic monomers" means monomers which form substantially water insoluble homopolymers.

Nonlimiting classes of monomers useful herein include monomers selected from the group consisting of unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated dicarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.

Representative examples of such monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-

1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-tri methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; dicyclopentenyl acrylate; 4-biphenyl acrylate; pentachlorophenyl acrylate; 3,5-dimethyladamantyl acrylate; 3,5-dimethyladamantyl methacrylate; 4-methoxycarbonylphenyl methacrylate; trimethylsilyl methacrylate; styrene; alkyl substituted styrenes including alpha-methylstyrene and t-butylstyrene; vinyl esters, including vinyl acetate, vinyl neononanoate, vinyl pivalate and vinyl propionate; vinyl chloride; vinylidene chloride; vinyl toluene; alkyl vinyl ethers, including isobutyl vinyl ether and s-butyl vinyl ether; butadiene; cyclohexadiene; bicycloheptadiene; 2,3-dicarboxymethyl-1,6-hexadiene; ethylene; propylene; indene; norbornylene; β -pinene; α -pinene; salts of acids and amines listed above, and combinations thereof. The quaternized monomers can be quaternized either before or after the copolymerization with other monomers of the graft copolymer.

Preferred monomers include acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and mixtures thereof.

From the above descriptions, esters of acrylic and methacrylic acid that form low T_g homopolymers include, for example, 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, 2-phenoxyethyl ester, 2-hydroxyethyl

ester, 4-hydroxybutyl acrylate, 2-ethoxyethoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, n-ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate; Acrylamide monomers including N-dodecylacrylamide, N-octadecylacrylamide; Vinyl monomers including sec-butyl vinyl ether, butyl vinyl ether, vinyl propionate, vinyl butyrate, decylvinyl ether, methyl vinyl ether and Styrene monomers including 4-decylstyrene. Other monomers that form low Tg homopolymers include isobutylene, 1-butene, 5-methyl-1-hexene, olefinic monomers that could be hydrogenated post polymerization (after formation of copolymers), for example, isoprene, 1,2-butadiene, 1,4-butadiene.

Preferred monomers which form low Tg homopolymers include 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate, N-octadecylacrylamide.

Most Preferred monomers which form low Tg homopolymers include 2-methoxyethyl acrylate, n-butyl acrylate, ethyl acrylate. These low Tg monomers preferably have Tg of from about -70°C to about 25°C, more preferably from about -60°C to about 0°C and most preferably from about -60°C to about -20°C.

From the above descriptions, acrylic and methacrylic acids that form high Tg homopolymers include, for example, sec-butyl methacrylate, t-butyl acrylate, methyl methacrylate, isopropyl methacrylate, 2-t-butylaminoethyl methacrylate, dimethyl aminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, 4-biphenyl acrylate, pentachlorophenyl acrylate, 3,5-dimethyladamantyl acrylate, 3,5-dimethyladamantyl methacrylate,

isobornyl acrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate (silyl esters could be hydrolysed to form acrylic or methacrylic acids), acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids; Acrylamide & methacrylamide monomers including N-butylacrylamide, acrylamide, N-isopropylacrylamide, N-t-butylmethacrylamide; Vinyl monomers including: 2-vinylpyridine, 4-vinylpyridine, vinyl acetate, vinyl chloride, N-vinylcaprolactam, N-vinyl pyrrolidone, cyclohexyl vinyl ether, vinyl alcohol, vinyl imidazole; Styrene monomers including: styrene, 4-t-butylstyrene, 2-methoxystyrene, 4-acetylstyrene, styrene sulfonate. Other monomers that form high Tg homopolymers include: diallyldimethylammonium chloride, maleimides, crotonic acid, itaconic acid, maleic anhydrides, allyl alcohol, α -pinene, β -pinene, tert-butyl styrene, α -methyl styrene, indene, norbornene, norbornylene.

Preferred monomers which form high Tg homopolymers include: t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, dimethyl aminoethyl methacrylate, isopropyl methacrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene, α -methyl styrene, 2-vinylpyridine, 4-vinylpyridine, N-isopropylacrylamide, N-t-butylmethacrylamide.

Most Preferred monomers which form high Tg homopolymers include: t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene. These high Tg monomers preferably have Tg of from above about 25° C to about 250° C, more preferably from about 30° C to about 200° C, even more preferably from about 35° C to about 150° C, and most preferably from about 40° C to about 130° C.

Polysiloxane Macromonomer Units

The copolymers of the present invention comprise from about 2% to about 50%, preferably from about 5% to about 40%, and more preferably from about 10% to about 30%, by weight of the copolymer of polysiloxane macromonomer units.

The polysiloxane macromonomer units are copolymerizable with the vinyl monomers, said macromonomers preferably having a vinyl moiety. Either a single type of macromonomer unit or combinations or two or more macromonomer units can be utilized herein. The macromonomers are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the macromonomers can be reacted with or polymerized with the vinyl monomers in a polymerization reaction using one or more conventional synthetic techniques, as described above.

The polysiloxane macromonomers that are useful herein contain a polymeric portion and a copolymerizable moiety which is preferably an ethylenically unsaturated moiety. Typically, the preferred macromonomers are those that are endcapped with the vinyl moiety. By "endcapped" as used herein is meant that the vinyl moiety is at or near a terminal position of the macromonomer.

The macromonomers can be synthesized utilizing a variety of standard synthetic procedures familiar to the polymer chemist of ordinary skill in the art. Furthermore, these macromonomers can be synthesized starting from commercially available polymers. Typically, the weight average molecular weight of the macromonomer is from about 1000 to about 50,000.

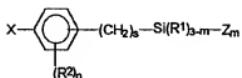
Polysiloxane macromonomers are exemplified by the general formula:



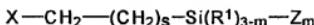
wherein X is a vinyl group copolymerizable with the vinyl monomer units; Y is a divalent linking group; each R is independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. The polysiloxane macromonomer has a weight average molecular weight from

about 1000 to about 50,000, preferably from about 5,000 to about 30,000, more preferably from about 8,000 to about 25,000.

Preferably, the polysiloxane macromonomer has a formula selected from the following formulas:



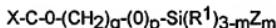
or



or

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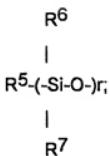


In these structures s is an integer from 0 to 6; preferably 0, 1, or 2; more preferably 0 or 1; m is an integer from 1 to 3, preferably 1; p is 0 or 1; q is an integer from 2 to 6; each R¹ is independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, preferably C1-C6 alkyl, or C1-C6 alkyl or alkoxy-substituted phenyl, more preferably C1-C6 alkyl, even more preferably methyl, R² is selected from the group consisting of C1-C6 alkyl or C1-C6 alkyl substituted phenyl, preferably methyl.

n is an integer from 0 to 4, preferably 0 or 1, more preferably 0; X is



wherein R³ is hydrogen or -COOH, preferably R³ is hydrogen; R⁴ is hydrogen, methyl or -CH₂COOH, preferably R⁴ is methyl; Z is



wherein R⁵, R⁶, and R⁷, are independently selected from hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, hydrogen or hydroxyl, preferably R⁵, R⁶, and R⁷ are C1-C6 alkyls; more preferably methyl; and r is an integer of from about 14 to about 700, preferably about 60 to about 400, and more preferably about 100 to about 350.

Exemplary silicone grafted polymers for use in the present invention include the following, where the composition is given as weight part of monomer used in the synthesis:

- (i) poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)
MW_t of copolymer: 210,000
Composition: t-butyl acrylate (36%), n-butyl acrylate (27%), acrylic acid (12%), methacrylic acid (10%), poly(dimethylsiloxane) (15%)
MW_t of poly(dimethylsiloxane): 10,000
- (ii) poly(t-butyl acrylate-co-ethyl acrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)
MW_t of copolymer: 100,000
Composition: t-butyl acrylate (34%), ethyl acrylate (35%), acrylic acid (21%), poly(dimethylsiloxane) (10%)
MW_t of poly(dimethylsiloxane): 5,000
- (iii) poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 150,000

Composition: t-butyl acrylate (47.25%), n-butyl acrylate (22.75%), acrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 10,000

(iv) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 100,000

Composition: t-butyl acrylate (27%), 2-methoxyethyl acrylate (43%), methacrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 15,000

(v) poly(t-butyl acrylate-co-isobornyl acrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 95,000

Composition: t-butyl acrylate (33%), isobornyl acrylate (17%), 2-methoxyethyl acrylate (20%), acrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 10,000

(vi) poly(t-butyl acrylate-co-lauryl methacrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 125,000

Composition: t-butyl acrylate (60%), lauryl methacrylate (10%), acrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 15,000

The Tg's for monomer units above can be found in The Polymer Handbook, third edition, (John Wiley & Sons, 1989) and the backbone Tg can be calculated using the method illustrated in Fundamental Principles of Polymeric Materials, second edition (John Wiley & Sons, 1993). Representative Tg's for monomers in the exemplary silicone grafted

polymers described above are as follows: The Tg of t-butyl acrylate is 44.85°C; the Tg of n-butyl acrylate is -54.15°C; the Tg of acrylic acid is 105.85°C; the Tg of methacrylic acid is 227.85°C; the Tg of ethyl acrylate is -24.15°C; the Tg of lauryl methacrylate is -65.15°C; and the Tg of 2-methoxyethyl acrylate is -50.15°C.

The silicone grafted polymers can be synthesized by free radical polymerization of the polysiloxane-containing monomers with the non-polysiloxane-containing monomers. The synthetic procedures are in general the same as those described for the adhesive copolymer. The silicone macromer is added in to the reactor along with the "A" and "B" monomers, and the reaction proceeds as for the adhesive copolymer examples. Compared to the adhesive copolymer, it may be necessary to choose different solvents for the polymerization reaction, as apparent to one skilled in the art, to keep the monomers and polymers in solution throughout the polymerization.

Without being limited by theory, it is believed that in forming the above-described silicone grafted polymers, there is some polymer which does not incorporate the silicone graft; such polymers have a relatively low weight average molecular weight e.g., below 20,000.

Personal Care Carrier

The compositions of the present invention comprise from about 0.1% to about 99.9%, preferably from about 0.5% to about 99.0% and most preferably from about 1.0% to about 99.9% of a suitable personal care carrier. Suitable carriers are fully described in U.S. Patent 5,061,481 issued October 29, 1991 to Suzuki et al., incorporated by reference herein. For example, skin care carriers typically comprise oil-in-water emulsions.

Hair spray compositions typically comprise a polar solvent phase as a liquid vehicle for the silicone grafted polymer. The polar solvent phases comprise one or more polar solvents that are present in the hair care compositions at a level of from about 80% to about 99%, preferably from

about 85% to about 98%, more preferably from about 90% to about 95% of the total composition.

The polar solvents essential to the present compositions are selected from the group consisting of water, C₂-C₃ monohydric alkanols, and mixtures thereof. If present, C₃ alkanols, such as isopropanol, should be used at levels no greater than about 15% by weight of the composition, preferably no greater than about 12%, more preferably no greater than about 10%. High levels of C₃ monohydric alcohols are undesirable in the present compositions due to potential odor issues they can create. Preferred polar solvent phases contain water, ethanol, or mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50% by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the range of from 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the total composition.

In yet another aspect of this invention are provided hair styling products, such as hair spray compositions, which contain reduced levels of volatile organic solvents. A reduced volatile organic solvent hair spray composition of the present invention contains no more than 80% volatile organic solvents (which include, for example, alkanols but not water). As used herein, volatile organic solvents means solvents which have at least one carbon atom and exhibit a vapor pressure of greater than 0.1 mm Hg at 20°C.

In the reduced volatile organic solvent hair styling products hereof, the compositions generally comprise at least 10%, by weight, of water. It is also specifically contemplated that they may contain at least about 11%, 12%, 13%, 14%, 15%, or more water.

The reduced volatile organic solvent compositions hereof will comprise up to about 90%, preferably up to about 70%, more preferably up

to about 60% even more preferably no more than about 50%, water; and from about 10% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 80%, of volatile organic solvent. It is also contemplated that the compositions can be limited to containing no more than about 75%, 65%, 55%, or other levels of volatile organic solvents.

Shampoos and rinse compositions typically comprise a volatile, nonpolar, branched chain hydrocarbon and is safe for topical application to the skin and hair. The branched chain hydrocarbon solvent hereof is present at a level of from about 0.1% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 2% to about 8%, by weight of the composition. Also useful are low boiling point silicone oils.

The branched chain hydrocarbon solvent is characterized by a boiling point of at least about 105°C, preferably at least about 110°C, more preferably at least about 125°C, most preferably at least about 150°C. The boiling point is also generally about 260°C or less, preferably about 200°C or less. The hydrocarbon chosen should also be safe for topical application to the hair and skin.

The branched chain hydrocarbon solvents are selected from the group consisting of C₁₀-C₁₄ branched chain hydrocarbons, and mixtures thereof, preferably C₁₁-C₁₃ branched chain hydrocarbons, more preferably C₁₂ branched chain hydrocarbons. Saturated hydrocarbons are preferred, although it isn't necessarily intended to exclude unsaturated hydrocarbons.

Examples of suitable nonpolar solvents include isoparaffins of the above chain sizes. Isoparaffins are commercially available from Exxon Chemical Co. Examples include Isopar™ G (C₁₀-C₁₁ isoparaffins), Isopar™ H and K (C₁₁-C₁₂ isoparaffins), and Isopar™ L (C₁₁-C₁₃ isoparaffins). The most preferred nonpolar solvent are C₁₂ branched chain hydrocarbons, especially isododecane. Isododecane is commercially available from Preperse, Inc. (South Plainfield, NJ, USA) as Permethyl™ 99A.

Plasticizer

The compositions hereof can optionally contain a plasticizer for the silicone grafted polymer. Any plasticizer suitable for use in hair care products or for topical application to the hair or skin can be used. A wide variety of plasticizers are known in the art. These include acetyl triethylcitrate, triethylcitrate, glycerin, diisobutyl adipate, butyl stearate, and propylene glycol. Plasticizers are typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%.

Optional ComponentsAdhesive Polymer

The compositions of the present invention can comprise an additional adhesive polymer. The compositions hereof will generally comprise from about 0.1% to about 15%, preferably from 0.5% to about 8%, more preferably from about 1% to about 8%, by weight of the composition, of the adhesive polymer. It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive or film-forming properties to the composition and the composition can be formulated and effectively applied for its intended purpose. By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

The polymeric backbone is chosen such that it is compatible with the silicone adhesive styling polymer. By "compatible" is meant is that, when placed in a suitable solvent, the polymers form a stable solution, i. e., the polymers do not compete for solubility and therefore, cause no phase separation and when the solution is dried a uniform film is formed, with no macrophase separation of the two polymers. A suitable solvent is a solvent which substantially completely dissolves the non-silicone and silicone grafted polymers at the levels described herein. The polymer blend forms a relatively clear hairspray system (% transmittance at 450 nm is generally

greater than 80%). It is recognized that certain plasticizers can form cloudy films as well as incorrect neutralization levels. Therefore, this would fall outside this definition of compatibility. The compatibility can be tested by dissolving the adhesive polymer and the silicone grafted hair styling resin in a mutual solvent, and then evaporating the solvent to form a film. Incompatible polymers will form a cloudy film with poor mechanical properties, due to the large scale phase separation of the two polymers. Alternatively, after drying the polymer solution to a film, compatibility can be evaluated by measuring the Tg. Compatible polymers will have a single Tg, while incompatible polymers will exhibit two Tg's. Although compatibility can occur between two polymers of completely different structures, it is preferred that compatibility be obtained by making the composition of the non-silicone backbone of the silicone grafted polymer similar to or identical to the composition of the adhesive polymer.

The adhesive polymer should have a weight average molecular weight of at least about 20,000, preferably greater than about 25,000, more preferably greater than about 30,000, most preferably greater than about 35,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 2,000,000. Preferably, the weight average molecular weight will be between about 20,000 and about 2,000,000, more preferably between about 30,000 and about 1,000,000, and most preferably between about 40,000 and about 500,000.

Preferably, the adhesive hereof when dried to form a film have a Tg of at least about -20°C, more preferably at least about 20°C, so that they are not unduly sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the backbone of the

polymer. Preferably, the Tg is above about -20°C, more preferably above about 20°C.

Preferably the weight ratio of the non-silicone polymer to silicone grafted polymer ranges from about 1:10 to about 1:1, preferably from about 1:5 to about 1:1.

Exemplary adhesive polymers for use in the present invention include the following, where the numbers following the structure indicate the weight ratios of monomers as loaded into the polymerization reactor:

- (i) acrylic acid/t-butyl acrylate 25/75
- (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl-methacrylate 40/40/20
- (iii) t-butylacrylate/acrylic acid 65/35
- (iv) polymer (ii) quaternized by treatment with methyl chloride

The adhesive polymers can be synthesized as described above such as by free radical polymerization of the monomers.

Solubility of the adhesive polymer, as described above, should be determined after neutralization, if any, as well as after addition of other ingredients that may be included in the polar solvent phase, such as surfactants, solubilizers, etc.

The present compositions can contain a wide variety of additional optional ingredients, including among them any of the types of ingredients known in the art for use in hair setting compositions, especially hair spray compositions and hair setting tonics. These ingredients include, but are not limited to, surfactants (including fluorinated surfactants and silicone copolyols), and ionic strength modifiers, propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.)

Ionic Strength Modifier System

Optionally, the compositions of the present invention can contain an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the hair spray composition. When used, the ionic

strength modifiers will be present in the present compositions at a level of at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the polar liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH⁻ and H⁺ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof

are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in

the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The use of ionic strength modifiers are especially useful in reduced volatile organic solvent compositions, most especially those utilizing silicone macromer-containing polymers.

Personal Care Compositions

The present invention encompasses a wide variety of personal care compositions, including shampoos, soaps, lotions, creams, antiperspirants, nail enamels, lipsticks, foundations, mascaras, sunscreens, hair spray compositions, mousses, and hair setting tonics. Compositions that will be flowable, e.g., low viscosity compositions that, preferably, are suitable for spray application as well as higher viscosity compositions are also contemplated.

Personal care carriers are suitable for use in the present invention are described in U.S. Patent 5,306,485 to Robinson et al., issued April 26, 1994, and U.S. Patent 5,002,680 to Schmidt et al., issued March 26, 1991, both of which are incorporated by reference herein. Hair spray compositions and mousses of the present invention can be dispensed from containers which are aerosol dispensers or pump spray dispensers. Such dispensers, i.e., containers, are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants may be used to propel the compositions. A suitable propellant for use can be generally any liquefiable gas conventionally used for aerosol containers.

Suitable propellants for use are volatile hydrocarbon propellants which can include liquefied lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are

hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, N-butane, isobutane, propanes, nitrogen, carbon dioxide, nitrous oxide and atmospheric gas and mixtures thereof.

The aerosol propellant may be mixed with the present compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 40% by weight of the total composition.

Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other hair styling compositions include tonics and lotions, which are typically dispensed in a conventional bottle or tube, and applied directly to the hair or first dispensed to the hand and then to the hair.

The hair styling formulations of the present invention can optionally contain conventional hair care composition adjuvants. Generally, adjuvants

collectively can comprise from about 0.05% to about 5% by weight and preferably from about 0.1% to about 3%, by weight. Such conventional optional adjuvants are well known to those skilled in the art and include in addition to those discussed above, emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents; sunscreens; preservatives; thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

METHOD OF MAKING

The personal care compositions of the present invention can be made using conventional formulation and mixing techniques.

METHOD OF USE

The compositions of the present invention are used in conventional ways to provide the personal care compositions of the present invention. Such method generally involves application of an effective amount of the product. For example, in a hair spray composition, said composition is applied to the desired dry, slightly damp, or wet hair before and/or after the hair is arranged to a desired style. The composition is then dried or allowed to dry. By "effective amount" is meant an amount sufficient to provide the desired benefits.

The following Experimentals and Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

EXPERIMENTALS

The following synthesis exemplify silicone grafted polymers useful in the present compositions.

Polymer 1

Synthesis of Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

Place 42.75 parts of t-butyl acrylate, 27.25 parts n-butyl acrylate, 10 parts methacrylic acid, 10 parts acrylic acid, and 10 parts polydimethylsiloxane macromonomer in a roundbottom flask. Add sufficient acetone as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction to 58°C. Prepare a 10% solution of azobisisobutyronitrile (0.5% by weight relative to the amount of monomer) in acetone, and add it to the reaction mixture. Maintain heat and stirring for 20 hours. Terminate the reaction by opening the reactor to atmosphere and cooling to room temperature.

The polymer solution is then precipitated in water at one part solution to 15 parts water. The resultant polymer is then redissolved in acetone. This procedure is repeated six times, with the final polymer being placed in a vacuum oven for heated drying. This completes the polymer purification process.

Polymer 2

Synthesis of Poly(t-butyl acrylate-co-n-butyl acrylate-co-methacrylic acid)-graft-poly(dimethylsiloxane)

Place 32 parts of t-butyl acrylate, 27 parts n-butyl acrylate, 21 parts methacrylic acid, and 20 parts polydimethylsiloxane macromonomer in a roundbottom flask. Add sufficient acetone as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction to 58°C. Prepare a 10% solution of azobisisobutyronitrile (0.5% by weight relative to the amount of monomer) in acetone, and add it to the reaction mixture. Maintain heat and stirring for 20 hours. Terminate the

reaction by opening the reactor to atmosphere and cooling to room temperature.

The polymer solution is then precipitated in water at one part solution to 15 parts water. The resultant polymer is then redissolved in acetone. This procedure is repeated six times, with the final polymer being placed in a vacuum oven for heated drying. This completes the polymer purification process.

EXAMPLES

Examples 1-4

The following examples represent nonaerosol hairspray compositions of the present invention.

Component (wt. %)	1	2	3	4
Copolymer ¹	4.00	4.75	5.50	5.50
Isododecane ²	1.00	1.00	1.00	3.00
Diisopropyl butyl adipate	0.40	0.75	0.90	0.55
Sodium hydroxide ³	0.96	1.20	1.44	1.6
Perfume	0.10	0.10	0.10	0.10
Water	17.00	20.00	20.00	18.00
Ethanol ⁴	76.54	71.95	70.56	71.25

¹ Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane).

² PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

³ Sodium hydroxide is 30% active.

⁴ SDA 40 (100% ethanol).

EXAMPLE 5Sunscreen Composition

An oil-in-water emulsion is prepared by combining the following components utilizing conventional mixing techniques.

IngredientsPhase AWeight %

Water	QS100
Carbomer 954[1]	0.24
Carbomer 1342[2]	0.16
Copolymer[3]	1.00
Disodium EDTA	0.05

Phase B

Isoarachidyl Neopentanoate[4]	2.00
PVP Eicosene Copolymer[5]	2.00
Octyl Methoxycinnamate	7.50
Octocrylene	4.00
Oxybenzone	1.00
Titanium Dioxide	2.00
Cetyl Palmitate	0.75
Stearoxytrimethylsilane (and)	
Stearyl Alcohol[6]	0.50
Glyceryl Tribehenate	0.75
Dimethicone	1.00
Tocopheryl Acetate	0.10
DEA-Cetyl Phosphate	0.20

Phase C

Water	2.00
Triethanolamine 99%	0.60
NaOH solution 40%	0.33

Phase D

Water	2.00
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Butylene Glycol	2.00
DMDM Hydantoin (and)	
Iodopropynyl Butylcarbamate ^[7]	0.25
dL Panthenol	1.00
<u>Phase E</u>	
dimethylmyristamine	0.36

- [1] Available as Carbopol® 954 from B.F. Goodrich.
- [2] Available as Carbopol® 1342 from B.F. Goodrich.
- [3] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)
- [4] Available as Ganex V-220 from GAF Corporation.
- [5] Available as DC 580 Wax from Dow Corning.
- [6] Available as Synchrowax HRC from Croda.
- [7] Available as Glydant Plus from Lonza.

In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85°C. In a separate vessel the Phase B ingredients (except DEA-Cetyl Phosphate) are combined and heated to 85-90°C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The Phase C ingredients are combined until dissolved and then added to the emulsion. The emulsion is then cooled to 40-45°C with continued mixing. In another vessel, the Phase D ingredients are heated with mixing to 40-45°C until a clear solution is formed and this solution is then added to the emulsion. Finally, the emulsion is cooled to 35°C and the Phase E ingredients are combined at 65°C, use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. Phase E is cooled to 35°C, added and mixed.

This emulsion is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE 6Facial Moisturizer

A leave-on facial emulsion composition containing a cationic hydrophobic surfactant is prepared by combining the following components utilizing conventional mixing techniques.

<u>Ingredient</u>	<u>Weight %</u>
Phase A	
Water	QS100
Glycerin	3.00
Cetyl Palmitate	3.00
Cetyl Alcohol	1.26
Quaternium-22	1.00
Glyceryl Monohydroxy Stearate	0.74
Dimethicone	0.60
Stearic Acid	0.55
Octyldodecyl Myristate	0.30
Potassium Hydroxide	0.20
Carbomer 1342	0.125
Tetrasodium EDTA	0.10
DMDM Hydantoin and Iodopropynyl	
Butyl Carbamate	0.10
Carbomer 951	0.075
Phase B	
Isododecane	4.00
Copolymer[1]	1.00
stearamine	0.36

[1] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

In a suitable vessel the Phase A ingredients are combined to form an emulsion. Phase B is prepared by dispersing the copolymer in Isododecane (solvent) then adding the stearamine. Heat the solution to 65°C and use an

appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. Cool the Phase B and mix into Phase A using conventional mixing techniques.

This emulsion is useful for application to the skin as a moisturizer.

EXAMPLE 7

The following is an anti-perspirant composition representative of the present invention.

Component	Weight %
PPG 2 Myristyl Propionate	34.00 %
Glyceryl C ₁₈ - C ₃₆ Wax Acid Ester	0.40 %
Cyclomethicone	32.75 %
Copolymer[1]	1.00 %
dimethylmyristamine	0.50 %
Aluminum Chlorohydrate	19.00 %
PPG 5 Ceteth 20	7.50 %
Water	1.50 %

[1] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

Mix PPG 2 Myristyl Propionate and Glyceryl C₁₈ - C₃₆ Wax Acid Ester, heat to 75°C. Disperse the Chlorohydrate. Disperse the copolymer in Cyclomethicone (solvent) then add the dimethylmyristamine. Heat the solution to 65°C and use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. Add the cyclomethicone mixture to the Chlorohydrate dispersion. Mix PPG 5 Ceteth 20 and the water, then add to oils, perfume and cool.

EXAMPLE 8

The following is an anti-acne composition representative of the present invention.

Component	Weight %
<u>Copolymer-Solvent Mix</u>	
Copolymer[1]	1.00 %
dimethylpalmitamine	0.18 %
Isopar H® [2]	3.75 %
<u>Main Mix</u>	
Water	Q.S. to 100 %
Ethanol (SDA 40)	40.00 %
Carbopol 940®	0.75 %
Triethanol Amine	1.00 %
Salicylic Acid	2.00 %

[1]Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

[2]C₁₁-C₁₂ Isoparaffin, available from Exxon Chemical Co.

This product is prepared by dispersing the copolymer in Isopar H® (solvent) then adding the dimethylpalmitamine. Heat the solution to 65°C and use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. The other components are mixed in a separate vessel at ambient temperature. The copolymer-solvent premix is cooled (if needed) and added to the other components. This composition is useful for application to the skin to provide improved water resistance and is useful in the treatment of acne.

EXAMPLE 9

The following is an anti-acne composition representative of the present invention.

Component	Weight %
<u>Copolymer-Solvent Mix</u>	
Copolymer[1]	1.00 %
dimethylpalmitamine	0.18 %
Isopar H® [2]	3.75 %
<u>Main Mix</u>	
Water	Q.S. to 100 %
Ethanol (SDA 40)	20.00 %
Carbopol 940®	0.75 %
Triethanol Amine	1.00 %
Ibuprofen	2.00 %

[1]Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

[2] C₁₁-C₁₂ Isoparaffin, available from Exxon Chemical Co.

This product is prepared by dispersing the copolymer in Isopar H® (solvent) then adding the dimethylpalmitamine. Heat the solution to 65°C and use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. The other components are mixed in a separate vessel at ambient temperature. The copolymer-solvent premix is cooled (if needed) and added to the other components. This composition is useful for application to the skin to provide improved water resistance and is useful for the analgesic effects.

WHAT IS CLAIMED IS:

1. A personal care composition comprising:
 - (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises
 - (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and
 - (ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25°C to about 250°Cwherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and
 - (b) a personal care carrier.
2. A personal care composition according to Claim 1, wherein said monomer of (a) and (b) is independently selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, esters of C₁-C₁₈ alcohols, styrene; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-

methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene and salts of acids and amines above.

3. A personal care composition according to Claim 2 wherein the monomer of (a) is selected from the group consisting of 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, 2-phenoxyethyl ester, 2-hydroxyethyl ester, 4-hydroxybutyl acrylate, 2-ethoxyethoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, n-ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate, N-dodecylacrylamide, N-octadecylacrylamide, sec-butyl vinyl ether, butyl vinyl ether, vinyl propionate, vinyl butyrate, decylvinyl ether, methyl vinyl ether, 4-decylstyrene, isobutylene, 1-butene, 5-methyl-1-hexene, isoprene, 1,2-butadiene, 1,4-butadiene and mixtures thereof.
4. A personal care composition according to Claim 3 wherein the monomer of (a) is selected from the group consisting of 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate, N-octadecylacrylamide and mixtures thereof.

5. A personal care composition according to Claim 4 wherein the monomer of (a) is selected from the group consisting of 2-methoxyethyl acrylate, n-butyl acrylate, n-ethyl acrylate and mixtures thereof.
6. A personal care composition according to Claim 3 wherein the monomer of (a) has a Tg of from about -70° C to about 25° C.
7. A personal care composition according to Claim 6 wherein the monomer of (a) has a Tg of from about -60° C to about 0° C.
8. A personal care composition according to Claim 7 wherein the monomer of (a) has a Tg of from about -60° C to about -20° C.
9. A personal care composition according to Claim 2 wherein the monomer of (b) is selected from the group consisting of sec-butyl methacrylate, t-butyl acrylate, methyl methacrylate, isopropyl methacrylate, 2-t-butylaminoethyl methacrylate, dimethyl aminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, 4-biphenyl acrylate, pentachlorophenyl acrylate, 3,5-dimethyladamantyl acrylate, 3,5-dimethyladamentyl methacrylate, isobornyl acrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, N-butylacrylamide, acrylamide, N-isopropylacrylamide, N-t-butylmethacrylamide, 2-vinylpyridine, 4-vinylpyridine, vinyl acetate, vinyl chloride, N-vinylcaprolactam, N-vinyl pyrrolidone, cyclohexyl vinyl ether, vinyl alcohol, vinyl imidazole, styrene, 4-t-butylstyrene, 2-methoxystyrene, 4-acetylstyrene, styrene sulfonate, diallyldimethylammonium chloride, maleimides, crotonic acid, itaconic acid, maleic anhydrides, allyl alcohol, α -pinene, β -pinene, tert-butyl

styrene, α -methyl styrene, indene, norbornene, norbornylene and mixtures thereof.

10. A personal care composition according to Claim 9 wherein the monomer of (b) is selected from the group consisting of t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, dimethyl aminoethyl methacrylate, isopropyl methacrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene, α -methyl styrene, 2-vinylpyridine, 4-vinylpyridine, N-isopropylacrylamide, N-t-butylmethacrylamide and mixtures thereof.
11. A personal care composition according to Claim 10 wherein the monomer of (b) is selected from the group consisting of t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene.
12. A personal care composition according to Claim 9 wherein the monomer of (b) has a Tg of from above about 30° C to about 200° C.
13. A personal care composition according to Claim 12 wherein the monomer of (b) has a Tg of from about 35° C to about 150° C.
14. A personal care composition according to Claim 11 wherein the monomer of (b) has a Tg of from about 40° C to about 130° C.

15. A personal care composition according to Claim 4 wherein said copolymer is formed from the random copolymerization of the following relative weight percentages of vinyl monomer units and polysiloxane-containing macromonomer units:
 - a. from about 50% to about 98%, by weight of said copolymer, of vinyl monomer units, and
 - b. from about 2% to about 50%, by weight of said copolymer, of polysiloxane-containing macromonomer units, wherein said polysiloxane-containing macromonomer units have a weight average molecular weight from about 1,000 to about 50,000, and correspond to the chemical formula:

$X(Y)_nSi(R)_{3-m}(Z)_m$ wherein:

X is a vinyl group copolymerizable with said vinyl monomer units;

Y is a divalent linking group;

R is selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl;

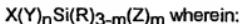
Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization;

n is 0 or 1; and

m is an integer from 1 to 3.

16. A personal care composition according to Claim 8 wherein said copolymer is formed from the random copolymerization of the following relative weight percentages of vinyl monomer units and polysiloxane-containing macromonomer units:
 - a. from about 50% to about 98%, by weight of said copolymer, of vinyl monomer units, and

b. from about 2% to about 50%, by weight of said copolymer, of polysiloxane-containing macromonomer units, wherein said polysiloxane-containing macromonomer units have a weight average molecular weight from about 1,000 to about 50,000, and correspond to the chemical formula:



X is a vinyl group copolymerizable with said vinyl monomer units;

Y is a divalent linking group;

R is selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alky or alkoxy-substituted phenyl;

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization;

n is 0 or 1; and

m is an integer from 1 to 3.

17. A personal care composition according to Claim 1 in the form of a shampoo, soap, lotion, cream, antiperspirant, nail enamel, lipstick, foundation, mascara, sunscreen, hair spray, mousse or hair setting tonic.

18. A hairspray composition comprising

(a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises

(i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and

(ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° C

wherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and

(b) a solvent carrier.

19. A hairspray composition according to Claim 17, wherein said monomer of (a) and (b) is independently selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, esters of C₁-C₁₈ alcohols, styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene and salts of acids and amines above and wherein the monomer of (a) has a Tg of from about -60° C to about -20° C .
20. A hairspray composition according to Claim 17 wherein the monomer of (b) is selected from the group consisting of sec-butyl methacrylate, t-butyl acrylate, methyl methacrylate, isopropyl methacrylate, 2-t-butylaminoethyl methacrylate, dimethyl aminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, 4-biphenyl acrylate, pentachlorophenyl acrylate, 3,5-dimethyladamantyl acrylate, 3,5-

dimethyladamentyl methacrylate, isobornyl acrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, N-butylacrylamide, acrylamide, N-isopropylacrylamide, N-t-butylmethacrylamide, 2-vinylpyridine, 4-vinylpyridine, vinyl acetate, vinyl chloride, N-vinylcaprolactam, N-vinyl pyrrolidone, cyclohexyl vinyl ether, vinyl alcohol, vinyl imidazole, styrene, 4-t-butylstyrene, 2-methoxystyrene, 4-acetylstyrene, styrene sulfonate, diallyldimethylammonium chloride, maleimides, crotonic acid, itaconic acid, maleic anhydrides, allyl alcohol, α -pinene, β -pinene, tert-butyl styrene, α -methyl styrene, indene, norbornene, norbornylene and mixtures therof and wherein the monomer of (b) has a Tg of from about 35° C to about 150° C.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/08285A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/48 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Category	Citation of document, with indication, where appropriate, of the relevant passages.	Relevant to claim No.
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X	WO 95 00106 A (PROCTER & GAMBLE :WELCH ROSEMARY JANE (GB); DODSWORTH EMMA LOUISE) 5 January 1995 see claim 8 -----	1-20
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International Application No

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INTERNATIONAL SEARCH REPORT

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(21) International Application Number: PCT/IB98/00753		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
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(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).			
(54) Title: PERSONAL CARE COMPOSITIONS CONTAINING GRAFT POLYMERS			
(57) Abstract			
<p>Disclosed are personal care compositions comprising from about 0.1 % to about 15 % by weight of a graft polymer and from about 0.1 % to about 99.9 % by weight of a liquid carrier, wherein the graft polymer is made in accordance with the following process steps: (a) reacting copolymerizable monomers to form an organic polymeric backbone having a weight average molecular weight of from about 15,000 grams/mole to about 200,000 grams/mole and a plurality of organic halide moieties covalently bonded to and pendant from the polymeric backbone; and then (b) reacting copolymerizable monomers with the organic halide moieties of the polymeric backbone by atom transfer free radical polymerization in the presence of a catalytic amount of a Cu(I) salt or other transition metal species to form a plurality of polymeric side chains covalently bonded to and pendant from the polymeric backbone and having a weight average molecular weight of from about 500 grams/mole to about 200,000 grams/mole, wherein the polymeric back bone and the plurality of polymeric side chains form hydrophilic and hydrophobic graft polymers suitable for use in personal care compositions and having a weight average molecular weight of from about 16,000 grams/mole to about 10,000,000 grams/mole.</p>			

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PERSONAL CARE COMPOSITIONS CONTAINING GRAFT POLYMERS

TECHNICAL FIELD

The present invention relates to an improved method of making hydrophobic and hydrophilic graft polymers suitable for use in personal care compositions, and to hair styling compositions and other personal care compositions containing the graft polymers.

BACKGROUND OF THE INVENTION

Personal care compositions such as hair sprays, styling shampoos, cosmetics, skin care products, and the like, often contain film-forming polymers for various reasons. These film-forming polymers are especially useful in hair care compositions to provide hair styling performance to the composition. Film-forming polymers for use in such compositions include organic or silicone-containing, linear or graft, copolymers which contain various monomers in an alternating, random, block or homopolymer configuration.

Graft copolymers are well known for use as film-forming polymers in hair care and other personal care compositions. These graft copolymers typically comprise a polymeric backbone and one or more macromonomers grafted to the backbone, wherein the physical and chemical attributes such as glass transition temperature values (Tg), water solubility, and so forth are selected for the polymeric backbone and macromonomer grafts so as to provide the desired film-forming properties and other chemical or physical properties of the copolymers in a personal care composition. The graft copolymers are especially versatile in that the polymeric backbone and the attached macromonomer grafts can have select or different chemical or physical properties which collectively provide the optimal formulation or performance profile for the intended personal care composition in which it will be used.

Synthesis of graft copolymers, however, is typically more difficult than synthesis of many copolymers, especially linear polymers. Unlike linear polymer synthesis, the synthesis of graft copolymers typically involves a separate polymerization step involving the making of a macromonomer containing a reactive end group, copolymerization of the macromonomer with a copolymerizable,

ethylenically unsaturated monomer, and then termination of this last copolymerization step to obtain the desired graft polymers.

It has now been found that hydrophobic and hydrophilic graft polymers can now be made by simpler, more effective synthesis methods, and that these new synthesis methods result in the formation graft polymers which when applied to the hair or other surface form a polymeric film or weld having improved adhesive and cohesive strength. These polymers are very useful when used as film-forming polymers in personal care compositions, especially when used as film-forming or styling polymers in hair styling compositions. The graft polymers in these hair styling compositions provide improved styling and/or conditioning performance, and are especially effective in providing improved durability of hair style and improved hair feel.

It is therefore an object of the present invention to provide an improved method for making graft polymers, and further to provide such a method for making graft polymers for use in personal care compositions, and yet further to provide such a method which involves fewer synthesis steps than other conventional methods of making graft polymers. It is yet another object of the present invention to provide hair styling and other personal care compositions containing the graft polymers made in accordance with the synthesis method herein, wherein the graft polymers have a low polydispersity, and wherein the compositions contain low or reduced concentrations of polymer contaminants such as ungrafted polymeric backbone and/or unattached polymeric grafts or side chains.

SUMMARY OF THE INVENTION

The present invention personal care compositions comprising from about from about 0.1% to about 15% by weight of a graft polymer and from about 0.1% to about 99.9% by weight of a liquid carrier, wherein the graft polymer is made in accordance with the process comprising the steps of (a) reacting copolymerizable monomers to form an organic polymeric backbone having a weight average molecular weight of from about 15,000 grams/mole to about 9,800,000 grams/mole and a plurality of organic halide moieties covalently bonded to and pendant from the polymeric backbone; and then (b) reacting copolymerizable monomers with the organic halide moieties of the polymeric backbone by atom transfer free radical polymerization in the presence of a catalytic amount of a transition metal species, preferably a Cu(I) salt and preferably complexed to a suitable ligand, to form a plurality of polymeric side chains covalently bonded to and pendant from the polymeric backbone and having a weight average molecular weight of from about

500 grams/mole to about 200,000 grams/mole, wherein the polymeric back bone and the plurality of polymeric side chains form graft polymers suitable for use in personal care compositions and having a weight average molecular weight of from about 16,000 grams/mole to about 10,000,000 grams/mole.

It has been found that the above-described process limitations allow for a simpler, more effective, synthesis of graft polymers using fewer process steps than conventional synthesis methods, and also allows for the synthesis of graft polymers without reliance upon the use of copolymerizable macromonomers, or a separate synthesis step for making such macromonomers. It has also been found that personal care compositions containing these graft polymers contain low or reduced concentrations of polymer contaminants such as ungrafted polymeric backbone and/or unattached polymeric grafts or side chains, wherein the graft polymers also have a low or reduced polydispersity.

DETAILED DESCRIPTION OF THE INVENTION

The process limitations of present invention comprise two key reaction steps. In a first reaction step, copolymerizable monomers are reacted together to form a polymeric backbone containing organic halide moieties covalently bonded to and pendant from the backbone. In a second subsequent reaction step, the polymeric backbone is reacted with copolymerizable monomers by atom transfer radical polymerization in the presence of a catalytic amount of a Cu(I) salt or other transition metal species, preferably complexed to a suitable ligand. Each of these two essential process steps are described in detail hereinafter.

The terms "hydrophilic" or "water soluble" as used herein, unless otherwise specified, are used interchangeably and refer to polymers (or salt forms of such polymers produced by neutralization or quaternization of acidic or basic groups) or other materials that are soluble in distilled water, ethanol, *n*-propanol, isopropanol, or combinations thereof, at 25°C and at a concentration of 0.2% by weight of such polymer or other material. The terms "hydrophobic" and "water insoluble" as used herein, unless otherwise specified, are used interchangeably and refer to all other polymers or materials that are not hydrophilic as defined herein.

The method of the present invention can comprise, consist of, or consist essentially of the essential elements or limitations of the invention described herein, as well as any of the additional or optional elements or limitations described herein.

All molecular weights as used herein, unless otherwise specified, are weight average molecular weights expressed as grams/mole.

All percentages, parts and ratios are by weight of the total referenced composition, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include solvents or by-products that may be included in commercially available materials, unless otherwise specified.

Synthesis Method

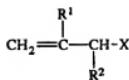
The personal care compositions of the present invention comprise graft polymers made in accordance with the process limitations herein, which process comprises two essential reaction steps. In the first reaction step, the polymeric backbone of the graft polymers herein are first prepared. This is accomplished by reacting copolymerizable monomers to form a polymeric backbone containing a plurality of organic halide moieties covalently bonded to and pendant from the polymeric backbone, and includes those polymers which conform generally to the formula



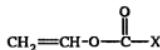
where "A" is a monomer unit having an organic halide moiety "C" attached which is covalently bonded to and pendant from the "A" monomer unit, and "B" is a monomer unit that is copolymerizable with the "A" monomer unit, "a" is a positive integer having a value of 2 or greater, preferably a value of from about 2 to about 30, and "b" is a positive integer having a value of at least about 4, preferably a value of from about 10 to about 2000. The organic halide moiety "C" includes any linear, branched or cyclic (aromatic or otherwise) carbon structure, whether substituted or unsubstituted, which also contain a halogen atom (Fl, Cl, Br or I).

In the first reaction step of the synthesis method herein, the "A" monomer unit with the attached organic halide moiety "C" is preferably selected from the group of allyl monomers, vinyl acetate monomers, acid halide monomers, styryl monomers, or combination thereof, and more preferably selected from the monomer units characterized by the following general structures (Groups I-V):

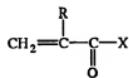
(I)



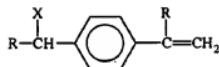
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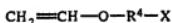
(III)



(IV)



(V)



where R is methyl or hydrogen; X is a halogen atom (Fl, Cl, Br, I); R¹ and R² are each independently selected from methyl, hydrogen or methoxy; and R⁴ is an alkyl group having from 1 to 8 carbon atoms.

The first reaction step of the process herein involves any conventional or otherwise known polymerization techniques such as ionic, Ziegler-Natta, free radical, group transfer or step growth polymerization, or combinations thereof. The first reaction step preferably involves conventional free radical polymerization techniques. Once the first reaction is complete, or has progressed to the extent desired, the first reaction step is terminated or allowed to terminate depending on the polymerization method selected, the degree or extent of polymerization desired, the reactivity of the monomer units selected for use in the reaction, and so forth. Any conventional or otherwise known termination technique appropriate for the selected reaction and reaction conditions may be used. For example, and most typically, after polymerization of the polymeric backbone by free radical polymerization, the

reaction mixture is heated to about 120°C for about 15 minutes to consume or react any remaining free radical initiator, and thereafter the reaction mixture is cooled or allowed to cool to room temperature to allow the reaction to self terminate before addition of ingredients to start the second reaction step.

In the second reaction step of the process of the present invention, the polymeric backbone described hereinabove is reacted with one or more copolymerizable monomers in the presence of a catalytic amount of a transition metal salt, preferably a Cu(I) salt and preferably complexed to a suitable ligand. In this reaction step, the organic halide moieties act as initiators in the presence of the copolymerizable monomers and the catalyst, resulting in the grafting of the monomers onto the polymeric backbone by atom transfer free radical polymerization, the monomers forming a plurality of polymeric side chains covalently bonded to and pendant from the backbone. The polymeric side chains form on the polymeric backbone without the need to use copolymerizable macromonomers to achieve the pendant polymeric graft chains.

The catalyst for the second reaction step is a transition metal salt, preferably a Cu(I) salt such as Cu(I) halide salts (Cl, Fl, Br, I) and which is preferably complexed to a ligand which is suitable for solubilizing the Cu(I) salt in the reaction mixture, wherein the reaction mixture of the second reaction step comprises dissolved or partially dissolved polymer, unreacted monomer, solvent and catalyst. Preferred ligands for use in solubilizing the Cu(I) salts in the reaction mixture are aprotic bidentates such as diphosphates, 2,2' bipyridyl, C1-C20 alkyl substituted bipyridyl and combinations thereof. Most preferred is 2,2' bipyridyl complexed to a Cu(I) halide salt, especially Cu(I) Cl. Other conventional or otherwise known ligands can be used herein provided that they do not substantially and unduly impair the polymerization reaction of the process herein, some examples of which are described in "The Use of Living Radical Polymerization to Synthesize Graft Copolymers" Dept. of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania; Simion Cocoa and Krzysztof Matyjaszewski, Polymer Preprints, Vol. 37(1), pg. 571-572, 1996. "Alternating Copolymers of Methyl Acrylate with Isobutene and Isobutyl Vinyl Ether using ATRP" Dept. of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania; Timothy e. Patten et al. Polymer Preprints, Vol. 37(1), pg. 573-574, 1996., "Radical Polymerization yielding Polymers with $M_w/M_n \sim 1.05$ by Homogeneous Atom Transfer Radical Polymerization" Carnegie Mellon University, Pittsburgh, Pennsylvania; T.E. Patten et al. Polymer Preprints, Vol. 37(1), pg. 575-576, 1996. "The Synthesis of End Functional Polymers by Living Radical Polymerization" Carnegie Mellon University, Pittsburgh, Pennsylvania, Y. Nakagawa

et al., *Polymer Preprints*, Vol. 37(1), pg. 577-578, 1996, which publications are incorporated herein by reference.

Graft Polymers

The process limitations of the present invention are especially useful for making hydrophobic or hydrophilic, film-forming polymers suitable for use in personal care compositions such as hair styling compositions. Graft polymers made in accordance with these process limitations typically have a low or reduced polydispersity and contain reduced concentrations of polymer contaminants such as ungrafted polymeric backbone and/or unattached polymeric grafts or side chains once the two step reaction steps of the synthesis are complete.

Graft polymers made in accordance with the synthesis method herein are characterized by a hydrophilic or hydrophobic polymeric backbone with a plurality of hydrophobic or hydrophilic polymeric side chains covalently bonded to and pendant from the polymeric backbone, wherein the polymeric backbone represents from about 50% to about 99%, preferably from about 60% to about 98%, more preferably from about 75% to about 95%, by weight of the graft polymer, and the plurality of polymeric side chains represent from about 1% to about 50%, preferably from about 2% to about 40%, more preferably from about 5% to about 25%, by weight of the graft polymer.

The polymeric side chains on the graft polymers have a weight average molecular weight of at least about 500 grams/mole, preferably from about 1,000 grams/mole to about 200,000 grams/mole, more preferably from about 1,500 grams/mole to about 30,000 grams/mole, most preferably from about 3,000 grams/mole to about 25,000 grams/mole. These polymeric side chains may comprise monomer units arranged in an alternating, random, block or homopolymer configuration, and each of the polymeric side chains may comprise the same or different monomers, arranged in the same or different configuration.

The graft polymers made in accordance with the synthesis method herein have a weight average molecular weight of from about 16,000 grams/mole to about 10,000,000 grams/mole, preferably less than about 5,000,000 grams/mole, more preferably less than about 3,000,000. Most preferred are weight average molecular weights of from about 50,000 grams/mole to about 2,000,000 grams/mole, more preferably from about 75,000 grams/mole to about 1,000,000 grams/mole, and even more preferably from about 75,000 grams/mole to about 750,000 grams/mole.

The graft polymers made in accordance with the synthesis method herein can have a single Tg value and preferably are copolymers having at least two distinct

immiscible phases, wherein the polymeric side chains are closely associated with each other and exist in one phase and the polymeric backbone of the copolymer remains in a second separate phase. A consequence of this phase immiscibility is that if the temperature separation between each of the Tg values involved is large enough then these copolymers exhibit two distinct glass transition temperatures, namely one Tg value for the backbone and one Tg value for the side chain. The copolymers can also exhibit a third glass transition temperature corresponding to any optional polysiloxane side chains on the graft copolymers. Whether such a third Tg value is observable depends upon a number of factors including the percent silicone in the copolymer, the number of polysiloxane side chains in the copolymer, the temperature separation between each of the Tg values involved, and other such physical factors.

The graft polymers made in accordance with synthesis method herein also preferably have a polydispersity of less than about 10, preferably less than about 5, even more preferably less than about 4.

Monomers suitable for use in the synthetic method herein can be hydrophilic or hydrophobic. In this context, the term "hydrophobic monomers" are those copolymerizable monomers which when reacted together form hydrophobic or water insoluble homopolymers, and the term "hydrophilic monomers" refers to those copolymerizable monomers which when reacted together form hydrophilic or water soluble homopolymers.

Monomers suitable for use herein must be copolymerizable and have the requisite characteristics defined herein for use in the synthetic method. These copolymerizable monomers are preferably ethylenically unsaturated monomers, more preferably copolymerizable vinyl monomers. The term "copolymerizable" as used herein means that a material can be reacted with another material in accordance with the first and/or second polymerization reaction steps of the synthesis method herein, whichever is appropriate. The term "ethylenically unsaturated" as used herein refers to monomers that contain at least one polymerizable carbon-carbon double bond (which can be mono-, di-, tri-, or tetra-substituted).

Such copolymerizable monomers include the copolymerizable organic halide-containing monomers described hereinbefore, and also includes the monomer units that are reacted with the organic halide-containing monomers in the first reaction step of the synthesis method, and also includes the monomer units that are reacted with the polymeric backbone in the second reaction step of the synthesis method.

Copolymerizable monomers for use in the first and second reaction steps of the synthesis method may be the same, or may include combinations of two or more different but copolymerizable monomers, including combinations of hydrophilic and

hydrophobic monomers, combinations of copolymerizable monomers having different but select glass transition temperatures (Tg), combinations of polar and nonpolar monomers, and so forth, or combinations of two or more copolymerizable monomers from a single chemical class or otherwise having similar physical or chemical characteristics. The graft polymers may therefore comprise the same or different monomer units, and may therefore be classified as homopolymers, copolymers, terpolymers and so forth.

Nonlimiting classes of monomers useful herein include monomers selected from the group consisting of unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated dicarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.

Representative examples of such monomers include acrylic acid (produced by hydrolysis of trimethylsilyl acrylate), methacrylic acid (produced by hydrolysis of trimethylsilyl methacrylate), trimethylsilyl acrylate, trimethylsilyl methacrylate, acrylamide, acrylate alcohols produced by hydrolysis of trimethylsilyl protected alcohol, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-tri methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octa decanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; dicyclopentenyl acrylate; 4-biphenyl acrylate; pentachlorophenyl acrylate; 3,5-

dimethyladamantyl acrylate; 3,5-dimethyladamantyl methacrylate; 4-methoxycarbonylphenyl methacrylate; trimethylsilyl acrylate, trimethylsilyl methacrylate; styrene; alkyl substituted styrenes including alpha-methylstyrene and t-butylstyrene; vinyl esters, including vinyl acetate, vinyl neononanoate, vinyl pivalate and vinyl propionate; vinyl chloride; vinylidene chloride; vinyl toluene; alkyl vinyl ethers, including isobutyl vinyl ether and *s*-butyl vinyl ether; butadiene; cyclohexadiene; bicycloheptadiene; 2,3-dicarboxymethyl-1,6-hexadiene; ethylene; propylene; indene; norbornylene; β -pinene; α -pinene; salts of acids and amines listed above, and combinations thereof. The quaternized monomers can be quaternized either before or after the copolymerization with other monomers of the graft copolymer.

Preferred monomers include acrylic acid (produced by hydrolysis of trimethylsilyl acrylate), methacrylic acid (produced by hydrolysis of trimethylsilyl methacrylate), vinyl pyrrolidone, acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, trimethylsilyl acrylate, trimethylsilyl methacrylate, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, *n*-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof.

The suitable copolymerizable monomers described herein are meant to include those corresponding copolymerizable monomers that are unsubstituted or substituted with one or more substituent groups, provided that such groups do not unduly impair the polymerization reactions of the synthesis method. Examples of suitable substituent groups include, but are not limited to, alkyl, aryl, carboxyl, halo groups, and combinations thereof.

Specific examples of hydrophilic graft polymers made in accordance with the process limitations of the present invention include, but are not limited to,

Poly(2-methoxyethyl acrylate-co-methacrylic acid-co-tert-butyl acrylate-co-4-chloromethyl styrene)-graft-poly(styrene-co-methacrylic acid); molecular weight of 150,000 grams/mole, Composition : 2-methoxyethyl acrylate (31.6%), methacrylic acid (22%), tert-butyl acrylate (28%) 4-chloromethyl styrene (0.4%), styrene (18%)

Poly(2-methoxyethyl acrylate-co-methacrylic acid-co-tert-butyl acrylate-co-4-chloromethyl styrene)-graft-[poly(styrene-co-methacrylic acid);poly(dimethylsiloxane)]; molecular weight of 150,000 grams/mole, Composition : 2-methoxyethyl acrylate (26.6%), methacrylic acid (22%), tert-butyl acrylate (28%) 4-chloromethyl styrene (0.4%), poly(dimethylsiloxane) macromonomer (molecular weight 10,000 grams/mole) (5%) styrene (18%).

Poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-acrylic acid-co-4-chloromethyl styrene)-graft-poly(isobutyl methacrylate-co-methacrylic acid); molecular weight 80,000 grams/mole; Composition : t-butyl acrylate (22%), 2-methoxyethyl acrylate (31%), acrylic acid (18%), 4-chloromethyl styrene (1%), isobutyl methacrylate (15%), methacrylic acid (13%)

Poly(vinyl acetate-co-vinyl pyrrolidone-co-chlorovinyl acetate)-graft-poly(styrene-co-methacrylic acid); molecular weight 120,000 grams/mole; Composition : vinyl acetate (40%), vinyl pyrrolidone (39%), chlorovinyl acetate (1%), isobutyl methacrylate (10%), dimethylaminoethyl methacrylate (10%).

The hydrophilic graft polymers made in accordance with the synthesis methods herein may comprise acidic functionalities, such as carboxyl groups, and are usually used in at least partially neutralized form to promote solubility or dispersability of the polymer. In addition, use of the neutralized form aids in the ability of the hair styling compositions to be removed from the hair by shampooing. The extent of such neutralization ranges from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about 40% to about 85%, neutralization of the acidic functionalities of the graft polymer.

Neutralization of the hydrophilic graft polymers containing acidic functionalities may be accomplished by any conventional or otherwise known technique for affecting such neutralization by using an organic or inorganic base material. Metallic bases are particularly useful for this purpose. Suitable base neutralizers include, but are not limited to, ammonium hydroxides, alkali metal hydroxides, or an alkaline earth metal hydroxides, preferably potassium hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents include, but are not limited to, amines or amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA),

diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA) and dimethyl stearamine (DMS) and combinations thereof. Preferred are amines and metallic bases.

Neutralization of hydrophilic polymers containing basic functionalities, e.g., amino groups, are likewise preferably at least partially neutralized with an organic or inorganic acid e.g., hydrogen chloride. Neutralization can be accomplished by any conventional or otherwise known technique for accomplishing such neutralization. The preferred extent of neutralization is the same as that described for neutralization of acidic functionalities. Solubility for any neutralized graft polymer made in accordance with the synthesis method herein should be determined only after the desired acid or base neutralization.

Specific examples of hydrophobic graft polymers made in accordance with the process limitations of the present invention include, but are not limited to,

Poly(tert-butyl acrylate-co-2-ethylhexyl methacrylate-co-chloromethyl styrene)-graft-poly(n-butyl acrylate); molecular weight 100,000 grams/mole;
Composition: tert-butyl acrylate(54%), 2-ethylhexyl methacrylate (10%), 4-chloromethyl styrene (6%); n-butyl acrylate(30%)

Poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-4-chloromethyl styrene)-graft-poly(styrene); molecular weight 100,000 grams/mole;
Composition : t-butyl acrylate (25%), 2-methoxyethyl acrylate (50%), 4-chloromethyl styrene (2%), styrene(23%)

Poly(vinyl acetate-co-vinyl pyrrolidone-co-chlorovinyl acetate)-graft-poly(2-ethylhexyl acrylate); molecular weight 120,000 grams/mole;
Composition : vinyl acetate (40%), vinyl pyrrolidone (10%), chlorovinyl acetate (5%),
2-ethylhexyl acrylate.(45%)

Optional Silicone Grafts

The process limitations of the present invention may further comprise the copolymerization of silicone macromonomers with other copolymerizable monomers described herein during the first reaction step of the synthesis method of the present invention, to thus form a polymeric backbone comprising one or more silicone-grafted side chains and a plurality of organic halide moieties attached to and pendent from the polymeric backbone. The resulting silicone grafted polymeric backbone is

then subjected to the second reaction step of the process as described hereinbefore, thus producing graft copolymers comprising a plurality of nonsilicone-containing polymeric side chains in combination with one or more silicone-containing macromonomer grafts.

The optional silicone macromonomer is grafted to or polymerized into the polymeric backbone by any conventional or otherwise known method for making silicone graft copolymers. Most typically, these polymers are formed from the random copolymerization of vinyl or otherwise copolymerizable monomer units, some or all of which have attached organic halide moieties, and polysiloxane-containing macromonomer units containing a polymeric portion and a vinyl moiety copolymerizable with monomer units. Upon completion of polymerization, the siloxane polymeric portion of the macromonomer unit forms the polysiloxane side chains of the graft copolymer. The other copolymerizable monomer units and the vinyl portion of the macromonomer units form the polymeric backbone. The copolymerizable monomer and the polysiloxane-containing macromonomer can be selected from a wide variety of structures as long as the copolymer has the required properties described herein, including having the attached organic halide moieties which act as initiators in the second reaction step of the synthesis method herein.

Examples of related silicone graft copolymers, and methods of making them, are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. Additional silicone grafted polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al., filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991, which descriptions are incorporated herein by reference.

The silicone graft copolymers made in accordance with the synthesis methods herein may comprise from zero to about 50%, preferably from about 2% to about 40%, and more preferably from about 10% to about 30%, polysiloxane macromonomer units by weight of the graft polymer.

The polysiloxane macromonomer units are copolymerizable with the other selected monomers for use in the first reaction step of the synthesis method, the polysiloxane macromonomers having a vinyl or other copolymerizable moiety for

reaction with the other selected monomer. Either a single type of polysiloxane macromonomer unit or combinations of two or more polysiloxane macromonomer units can be used in the first reaction step. In this context, the term "copolymerizable" means that the polysiloxane macromonomers can be reacted with the other selected monomers, including the organic halide-containing monomers, in accordance with the first reaction step of the synthesis method herein, which results in the requisite polymeric backbone for use in the second reaction step of the synthesis method herein.

The polysiloxane macromonomers that are useful herein contain a polymeric portion and a copolymerizable moiety which is preferably an ethylenically unsaturated moiety. Typically, the preferred macromonomers are those that are endcapped with the vinyl moiety. By "endcapped" as used herein is meant that the vinyl moiety is at or near a terminal position of the macromonomer.

The polysiloxane macromonomers can be synthesized using a variety of conventional or otherwise known synthetic techniques familiar to the polymer chemist of ordinary skill in the art. Furthermore, these polysiloxane macromonomers can be synthesized starting from commercially available polymers. Typically, the weight average molecular weight of the polysiloxane macromonomer for use in the first reaction step is from about 1,000 grams/mole to about 50,000 grams/mole.

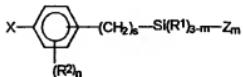
Polysiloxane macromonomers suitable for use herein include those which conform to the general formula:



wherein X is a vinyl group copolymerizable with the vinyl monomer units; Y is a divalent linking group; each R is independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, styryl, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000 and which is essentially unreactive under copolymerization conditions; n is an integer having a value of 0 or 1; and m is an integer having a value of from 1 to 3. The polysiloxane macromonomer has a weight average molecular weight from about 1,000 grams/mole to about 50,000 grams/mole, preferably from about 5,000 grams/mole to about 30,000 grams/mole, more preferably from about 8,000 grams/mole to about 25,000 grams/mole.

Preferably, the polysiloxane macromonomer has a formula selected from the following formulas I-III

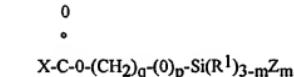
(I)



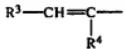
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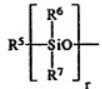
(III)



wherein s is an integer having a value of from 0 to 6; preferably 0, 1, or 2; more preferably 0 or 1; m is an integer having a value of from 1 to 3, preferably 1; p is an integer having a value of 0 or 1; q is an integer having a value of from 2 to 6; each R¹ is independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, preferably C1-C6 alkyl, or C1-C6 alkyl or alkoxy-substituted phenyl, more preferably C1-C6 alkyl, even more preferably methyl, R² is selected from the group consisting of C1-C6 alkyl or C1-C6 alkyl substituted phenyl, preferably methyl; n is an integer having a value of from 0 to 4, preferably 0 or 1, more preferably 0; X is



wherein R³ is hydrogen or -COOH, preferably R³ is hydrogen; R⁴ is hydrogen, methyl or -CH₂COOH, preferably R⁴ is methyl; Z is



wherein R⁵, R⁶, and R⁷, are independently selected from hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, styryl, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, hydrogen or hydroxyl, preferably R⁵, R⁶, and R⁷ are C1-C6 alkyls; more preferably methyl; and r is an integer having a value of from about 14 to

about 700, preferably about 60 to about 400, and more preferably about 100 to about 170.

Personal Care Compositions

The graft polymers made in accordance with the methods herein are especially useful when used as film-forming polymers in personal care compositions. Such compositions comprise the graft polymers made in accordance with the methods herein in combination with a suitable liquid carrier to dissolve or disperse, preferably dissolve, the graft polymer in the personal care composition.

The personal care compositions of the present invention include skin care compositions, styling or conditioning shampoo compositions, cosmetic compositions, or other similar compositions, many of which will further comprise one or more optional ingredients as described hereinafter. Preferred are hair care compositions such as conditioners, styling and/or conditioning shampoos, hair sprays, and styling mousse, tonics, gels or lotions. The film-forming graft polymer for use in such compositions, and which is made in accordance with the synthesis methods herein, provides the compositions with hair or skin conditioning performance or hair styling performance. The personal care compositions can be formulated as solids or liquids, single or multi-phase systems, emulsions, dispersions, solutions, gels, suspensions, or other formulation suitable for application to the skin or hair.

The personal care compositions of the present invention comprise the graft polymers made in accordance with the methods herein, at concentrations effective to provide the desired film-forming properties. Such concentrations generally range from about 0.1% to about 15%, preferably from about 0.5% to about 15%, even more preferably from about 0.5% to about 8%, even more preferably from about 1% to about 8%, by weight of the personal care composition, wherein the concentration of the liquid carrier generally ranges from about 85% to about 99.9%, preferably from about 92% to about 99.5%, even more preferably from about 92% to about 99%, by weight of the personal care composition.

The personal care compositions, especially when formulated as hair styling compositions, may be dispensed as sprayed or atomized liquids from pump spray or aerosol canisters. The aerosolized compositions comprise one or more conventional or otherwise known aerosol propellants. Suitable propellants include any liquifiable gas known or otherwise effective for use in this manner, examples of which include volatile hydrocarbon propellants such as liquified lower hydrocarbons having 3 or 4 carbon atoms such as propane, butane, isobutane, or combinations thereof. Other suitable propellants include hydrofluorocarbons such as 1,2-difluoroethane, and other

propellants such as dimethylether, nitrogen, carbon dioxide, nitrous oxide, atmospheric gas, and combinations thereof. Preferred are hydrocarbon propellants, particularly isobutane when used alone or in combination with other hydrocarbon propellants. Propellant concentrations should be sufficient to provide the desired delivery or application of the personal care composition to the hair or skin, which concentrations typically range from about 10% to about 60%, preferably from about 15% to about 50%, by weight of the composition.

Pressurized aerosol dispensers can also be used where the propellant is separated from contact with the hair styling composition, an example of which would be a two compartment canister available from the American National Can Corp. under the trade name SEPRO. Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patent 4,077,441, U.S. Patent 4,077,441 and U.S. Serial No. 07/839,648, which descriptions are incorporated herein by reference. Conventional non-aerosol pump spray dispensers or atomizers are also suitable for use herein.

A) Hydrophilic graft polymer compositions

The personal care compositions of the present invention preferably comprise a hydrophilic graft polymer made in accordance with the synthesis methods herein, and which is used in combination with a hydrophilic or water soluble or miscible liquid carrier suitable for solubilizing or dispersing the hydrophilic graft polymer in the personal care composition. These preferred compositions are especially useful when used as hair spray or other hair styling compositions.

Hydrophilic liquid carriers suitable for use herein include, but are not limited to, water, ethanol, *n*-propanol, isopropanol, and combinations thereof, preferably a combination of an alcohol and water wherein the water content of the composition ranges from about 0.5% to about 99%, preferably from about 0.5% to about 50%, by weight of the composition, and the alcohol content ranges from about 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the composition.

The hydrophilic graft polymers preferably have at least two distinct glass transition temperatures (T_g), the first of which is associated with the polymeric backbone and the second of which is associated with the plurality of polymeric side chains attached thereto. The polymeric backbone preferably has a T_g value of less than about 35 °C, more preferably less than about 25°C, even more preferably less than about 10°C, wherein the plurality of polymeric side chains have a T_g value

preferably greater than about 50°C, more preferably greater than about 60 °C, even more preferably greater than about 70°C.

Other suitable hydrophilic graft polymers made in accordance with the methods herein include those having a Tg value for the polymeric backbone of greater than about 30 °C, more preferably greater than about 40°C, even more preferably greater than about 50°C, wherein the plurality of polymeric side chains have a Tg value preferably of less than about 10°C, more preferably less than about 0 °C, even more preferably less than about -20°C.

These personal care compositions, especially when formulated as hair spray compositions, preferably contain reduced concentrations of volatile organic compounds, including volatile organic solvents. In this context, the volatile organic compounds or solvents are those organic compounds or solvents that contain less than 12 carbon atoms or have a vapor pressure greater than 0.1mm of mercury. Water concentrations in these preferred compositions are typically at least about 10% by weight of the composition, preferably from about 10% to about 50% by weight of the composition, wherein the concentration of the volatile organic compound or solvent is typically less than about 90%, preferably from about 20% to about 80%, more preferably from about 40% to about 70%, even more preferably from about 40% to about 60%, by weight of the composition.

B) Hydrophobic graft polymer compositions

Another embodiment of the personal care compositions of the present invention are those which comprise a hydrophobic graft polymer made in accordance with the synthesis methods herein, in combination with a hydrophobic or water insoluble liquid carrier suitable for solubilizing or dispersing or otherwise carrying the hydrophobic graft polymer in the personal care composition. These embodiments are especially useful when used as hair or skin conditioning compositions, some nonlimiting examples of which include skin care compositions, conditioning shampoos, and hair conditioners.

Suitable hydrophobic liquid carriers for the hydrophobic graft polymers include hydrophobic, volatile, liquids such as volatile branched chain hydrocarbons, silicones and combinations thereof. The concentration of such liquid carriers in the composition preferably range from about 0.1% to about 75%, more preferably from about 0.2% to about 25%, and even more preferably from about 0.5% to about 15%, by weight of the composition, wherein the weight ratio of hydrophobic graft polymer to the hydrophobic liquid carrier is generally from about 1:100 to about 5:1,

preferably from about 1:10 to about 1:1, more preferably from about 1:8 to about 2:3.

The hydrophobic liquid carrier is preferably a volatile liquid which exhibits a significant vapor pressure at ambient conditions (e.g., 1 atmosphere, 25°C). In this context, the term "volatile" refers to solvents or liquid carriers having a boiling point at one atmosphere of 260°C or less, preferably 250°C or less, more preferably 230°C or less, most preferably 225°C or less. In addition, the boiling point of the hydrophobic liquid carrier will generally be at least about 50°C, preferably at least about 100°C. The term "nonvolatile" as used in this context refers to solvents or liquid carriers which have a boiling point at one atmosphere of greater than 260°C.

The hydrophobic graft polymer is preferably soluble in the selected hydrophobic liquid carrier. In this context, the term "soluble" refers to the solubility of the hydrophobic graft polymer in the hydrophobic liquid carrier at 25°C at a concentration of 0.1%, preferably at 1%, more preferably at 5%, most preferably at 15%, by weight of the hydrophobic liquid carrier.

Preferred hydrophobic liquid carriers include hydrophobic, volatile, branched chain hydrocarbons, preferably saturated hydrocarbons, which contain from about 10 to about 16, preferably from about 12 to about 16, most preferably from about 12 to about 14, carbon atoms. Examples of such preferred branched chain hydrocarbons include isoparaffins of the above chain sizes. Isoparaffins are commercially available from Exxon Chemical Co.; examples include Isopar™ H and K (C₁₁-C₁₂ isoparaffins), and Isopar™ L (C₁₁-C₁₃ isoparaffins). Other suitable branched chain hydrocarbons are isododecane and isohexadecane. Isododecane is preferred and is commercially available from Preperse, Inc. (South Plainfield, NJ, USA) as Permethyl™ 99A.

Preferred hydrophobic silicone carriers include hydrophobic, volatile siloxanes (such as phenyl pentamethyl disiloxane, phenylethyl pentamethyl disiloxane, hexamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, cyclomethicones, including octamethyl cyclotetrasiloxane and decamethyl cyclopentasiloxane), and mixtures thereof. Preferred hydrophobic silicone solvents are cyclomethicones, more preferably octamethyl cyclotetrasiloxane and decamethyl cyclopentasiloxane.

It is understood that the hydrophobic liquid carriers can be used in combination with the hydrophilic liquid carriers in the personal care compositions, and that the hydrophobic graft polymers can likewise be used in combination with the hydrophilic graft polymers in the personal care composition. Such combinations are suitable for use in the personal care composition provided that they are physically and

chemically compatible with the selected ingredients in the composition, and do not otherwise substantially and unduly impair product performance.

Optional Ingredients

The personal care compositions described herein may further comprise one or more optional ingredients known or otherwise effective for use in hair styling compositions or other personal care compositions. These optional ingredients may be used to improve or otherwise modify aesthetics, performance or stability of the hair styling compositions. Concentrations of such optional ingredients will vary with the type of material added and its intended performance, but will typically and collectively range from about 0.005% to about 50%, more typically from about 0.05% to about 30% by weight of the composition.

Plasticizers for the graft copolymer are especially useful in the personal care compositions herein. Suitable plasticizers include any known or otherwise effective plasticizer suitable for use in hair care or other personal care compositions, nonlimiting examples of which include glycerin, diisobutyl adipate, butyl stearate, propylene glycol, tri-C₂-C₈ alkyl citrates, including triethyl citrate and tri-propyl, -butyl, -pentyl, etc., analogs of triethyl citrate. Triethyl citrate is preferred.

Plasticizers are typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%. Preferably, the weight ratio of graft polymer to the plasticizer is from about 1:1 to about 40:1, preferably from about 2:1 to about 30:1, more preferably from about 3:1 to about 25:1.

Other optional ingredients include an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the personal care composition, especially when formulated as a hair spray composition. Preferred concentrations range from at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the hydrophilic liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions

with more water. Concentrations of the optional ionic strength modifier are typically range from about 0.01% to about 4%, preferably from about 0.01% to about 2%, more preferably from about 0.01% to about 0.1%, by weight of the composition.

The optional ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The optional ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH⁻ and H⁺ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Nonlimiting examples of suitable optional cations for use in the compositions are alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, more preferably sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below. Other nonlimiting examples of suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and triethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The use of optional ionic strength modifiers are especially useful in reduced volatile organic solvent compositions.

Other optional ingredients include surfactants (which may be anionic, cationic, amphoteric, or zwitterionic and which include fluorinated surfactants and silicone copolyols), propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.); emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents; sunscreens; preservatives; thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

Method of Use

The personal care compositions of the present invention are used in conventional ways to provide the desired personal care benefit. For hair spray or other hair styling compositions, the composition is used in a conventional way to provide the desired hair styling/holding benefits of the present invention, which typically involves application of an effective amount of the composition to dry, slightly damp, or wet hair before and/or after the hair is arranged to a desired style. The composition is then dried or allowed to dry onto the applied surface.

The term "effective amount" as used in this context means an amount of the personal care composition or hair styling composition sufficient to provide the desired benefit. In the case of hair spray and other hair styling compositions, an effective amount of the composition is applied to the hair to provide the hold and style benefits desired considering the length and texture of the hair. In general, from about 0.5g to about 30g of such hair spray or other hair styling composition will be applied to the hair, depending upon the particular product formulation, dispenser type, length of hair, type of hair style, and so forth.

EXAMPLES

The following non-limiting examples illustrate specific embodiments of the process limitations of the present invention, graft polymers made in accordance with such process limitations, and hair styling and other personal care compositions comprising these graft polymers. It is understood, however, that various additions or modifications of the specific exemplified embodiments can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of the subject invention.

Example 1

The hydrophilic graft polymers 1.1 and 1.2 described in the following example are prepared in accordance with the process limitations of the present invention. Specific embodiments of such process limitations are described for each of the hydrophilic graft polymers.

Graft Polymer 1.1

Poly(2-methoxyethyl acrylate-co-methacrylic acid-co-tert-butyl acrylate-co-4-chloromethyl styrene)-graft-poly(styrene-co-methacrylic acid)

Into an argon purged round-bottomed-flask equipped with mechanical stirring and a reflux condenser, is added butyl acetate (1L), trimethylsilylmethacrylate (18.4g, 0.116 mole), tert-butylacrylate (27.2g, 0.212 mole), 2-methoxyethyl acrylate (31.4g, 0.241mole), and chloromethyl styrene (0.4g, 0.003 mole). The solution is heated to 60°C then initiated with AIBN (azobisisobutyronitrile) (0g, 0.006 mole) and allowed to undergo free radical polymerization for 10 hours. The resulting solution is then heated to 100°C and allowed to cool. When the solution reaches ambient temperature, trimethylsilylmethacrylate (22.0g, 0.139 mole), styrene (18.0g, 0.173mole), 2,2'-dipyridyl (1.4g, 0.009 mole), and Cu(I)Cl (0.3g, 0.003 mole) are added. The solution is then heated to 120°C with stirring for 6 hours. The solution is then cooled to ambient temperature and catalyst is removed via vacuum filtration. The filtrate is diluted with acetone (200 ml) and water (10 ml) and stirred for 2 hours. The resulting solution is precipitated into hexanes and the graft polymer collected and dried.

Graft Polymer 1.2

Poly(2-methoxyethyl acrylate-co-methacrylic acid-co-tert-butyl acrylate-co-4-chloromethyl styrene)-graft-[poly(styrene-co-methacrylic acid); poly(dimethylsiloxane)]

Into an argon purged round-bottomed-flask equipped with mechanical stirring and a reflux condenser, is added butyl acetate (1L), trimethylsilyl methacrylate (18.4g, 0.116 mole), tert-butylacrylate (27.2g, 0.212 mole), 2-methoxyethyl acrylate (26.4g, 0.203 mole), polydimethylsiloxane macromonomer (molecular weight 10,000)(available from Chisso Corp., Tokyo, Japan) (5g), and chloromethyl styrene (0.4g, 0.003 mole). The solution is heated to 60°C then initiated with AIBN (1.0g, 0.006 mole) and allowed to undergo free radical polymerization for 10 hours. The resulting solution is then heated to 100°C then allowed to cool. When solution reaches ambient temperature, trimethylsilylmethacrylate (22.0g, 0.139 mole), styrene (18.0g, 0.173mole), 2,2'-dipyridyl (1.4g, 0.009 mole), and Cu(I)Cl (0.3g, 0.003 mole) are added. The solution is heated to 120°C with stirring for 6h. The solution is then cooled to ambient temperature and catalyst is removed via vacuum filtration. Filtrate is diluted with acetone (200 ml) and water (10 ml) and stirred for 2 hours. The resulting solution is precipitated into hexanes and the graft polymer collected and dried.

Example 2

The hydrophobic graft polymer 2.0 described in the following example is prepared in accordance with the process limitations of the present invention. Specific embodiments of such process limitations are described for each of the hydrophobic graft polymers.

Graft Polymer 2.0

Poly(tert-butyl acrylate-co-2-ethylhexyl methacrylate-co-chloromethyl styrene)-graft-poly(n-butyl acrylate)

Into an argon purged round-bottomed-flask equipped with mechanical stirring and a reflux condenser, is added butyl acetate (1L), tert-butyl acrylate (54 g, 0.417 mole), 2-ethylhexyl methacrylate (10g, 0.050 mole), and chloromethyl styrene (6g, 0.039 mole). The solution is heated to 60 °C and then initiated with AIBN (0.6g,

0.004 mole) and allowed to undergo free radical polymerization for 12 hours. The resulting solution is heated to 100°C then allowed to cool. When solution reaches ambient temperature, n-butyl acrylate (30g, 0.211 mole), 2,2'-dipyridyl (18.3g, 0.117 mole), and Cu(I)Cl (3.9g, 0.039 mole) are added. The solution is heated to 120°C with stirring for 6 hours. The solution is then cooled to ambient temperature and catalyst is removed via vacuum filtration. The filtrate is diluted with acetone (200 ml) and water (10 ml) and stirred for 2 hours. The resulting solution is precipitated into hexanes and the graft polymer collected and dried.

Examples 3-10

The following Examples 3-10 represent nonaerosol hair spray embodiments of the compositions of the present invention.

	Example No.							
Component (wt%)	3	4	5	6	7	8	9	10
Graft copolymer 1.1	4.00	5.00	6.00	4.00	---	---	---	---
Graft copolymer 1.2	---	---	---	---	3.00	3.50	2.50	4.00
Isododecane ¹	1.00	---	---	---	---	1.0	2.0	---
Diisobutyl adipate	0.40	---	0.90	0.55	---	---	---	0.40
Sodium hydroxide ²	0.96	1.20	1.44	---	---	1.20	---	1.35
Potassium hydroxide ³	--	--	--	1.21	1.00	--	0.70	--
Perfume	0.10	0.10	0.10	0.10	0.10	0.15	0.10	0.15
Sodium Benzoate	--	--	--	--	0.10	0.10	--	0.10
Ethanol ⁴	76.54	71.95	81.56	71.25	79.40	69.26	78.00	55.00
Water	QS10	QS10	QS10	QS10	QS10	QS10	QS10	QS10
	0	0	0	0	0	0	0	0

¹ PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

² Sodium hydroxide is 30% active.

³ Potassium hydroxide is 45% active.

⁴ SDA 40 (100% ethanol).

Examples 11-16

The following Examples 11-16 represent aerosol hair spray embodiments of the compositions of the present invention.

Component (wt%)	Example No.					
	11	12	13	14	15	16
Graft copolymer 1.1	5.00	4.00	3.50	—	—	—
Graft copolymer 1.2	—	—	—	4.00	3.00	4.00
Isododecane ¹	0.50	—	—	—	—	0.50
Triethyl citrate ²	—	—	0.21	—	—	—
Diisobutyl adipate	0.70	0.45	—	0.40	0.25	0.35
Propylene glycol	—	—	0.30	—	—	—
Sodium hydroxide ³	1.00	—	—	—	1.0	—
Potassium hydroxide ⁴	—	0.94	1.20	1.04	—	1.20
Perfume	0.10	0.10	0.10	0.10	0.10	0.10
Sodium Benzoate	0.10	0.10	—	0.10	0.20	—
Ethanol ⁵	56.69	57.42	72.0	50.0	30.00	54.5
Propellant - isobutane	—	—	7.02	15.00	10.00	—
Propellant - n-butane	10.00	—	—	—	—	—
Propellant - dimethyl ether ⁶	10.00	—	—	15.00	15.00	—
Propellant -	—	25.0	15.98	—	—	32.32
Hydrofluorocarbon 152a ⁷	—	—	—	—	—	—
Water	QS100	QS100	QS100	QS100	QS100	QS100

1 PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

2 CITROFLEX-2, from Morflex, Inc., Greensboro, NC, USA.

3 Sodium hydroxide is 30% active.

4 Potassium hydroxide is 45% active.

5 SDA 40 (100% ethanol).

6 DYMEL - A, from Dupont.

7 DYMEL-152a, from Dupont.

Each of the exemplified personal care compositions (Examples 3-16) are hair spray or hair styling embodiments of the compositions of the present invention, and comprise graft polymer as a styling or film-forming polymer made in accordance with the synthetic methods of the present invention. Each of the compositions may be formulated by conventional or otherwise known formulation and mixing techniques. For example, each of the graft polymers is first mixed with the ethanol, neutralizing

the polymer with sodium or potassium hydroxide, then adding sequentially (as applicable) with mixing, isododecane, plasticizer, perfume, and water. If sodium benzoate is used, it is added after water addition. Most preferably a premix of water and sodium benzoate is made and then added after the main water addition. Propellants for aerosol compositions are charged to conventional aerosol containers after the remainder of the prepared composition has been added.

EXAMPLE 17

The following represents a hair styling gel embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.2	2.50
Water	QS 100%
Carbomer 940	0.50
Sodium Hydroxide Solution (30% by weight)	0.80
Panthenol	0.05
Polysorbate 80	0.20
Perfume	0.20

This product is prepared by dispersing graft copolymer and carbomer 940 in water and adding sodium hydroxide. The mixture is stirred for about 0.5 hour before adding the remaining ingredients.

EXAMPLE 18

The following represents a spray-on gel embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	Q.S. to 100 %
Ethanol	15.00
Panthenol	0.05
Potassium Hydroxide Solution (45% by weight)	0.50
Perfume	0.20
Graft copolymer 1.1	2.00

This composition is prepared by dissolving the graft copolymer 1.1 in ethanol and then adding water and potassium hydroxide solution to facilitate the

incorporation of the copolymer into the solvent. The mixture is stirred for about 0.5 hour before adding the remaining ingredients.

EXAMPLE 19

The following represents a hair styling mousse embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	Q.S. to 100 %
Lauramine Oxide	0.20
Panthenol	0.05
Perfume	0.05
Copolymer 1.2	3.00
Sodium Hydroxide Solution (30% by weight)	1.00
Isobutane	7.00

This composition is prepared by dissolving the graft copolymer 1.2 in water and then adding sodium hydroxide solution with mixing for about 0.5 hour. The other ingredients, except isobutane, are added and mixed for an additional 10 minutes. Aluminum aerosol cans are then filled with 93 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 7 parts Isobutane. This composition is useful for application to the hair to provide conditioning, styling and hold.

EXAMPLE 20

The following example represents a topical sun screen embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Water	QS100
Carbomer 1342 ^[1]	0.16
Octyl Methoxycinnamate	0.50
Dimethicone copolyol	0.10
Tocopheryl Acetate	0.10
Sodium Hydroxide (30% sol. by weight)	1.50
Ethanol	40.00
Copolymer 1.2	4.00

[1] Available as Carbopol® 1342 from B.F. Goodrich.

The water, ethanol, sodium hydroxide solution and polymer 4 are mixed for one half hour. The remaining ingredients are added and mixed for an additional half hour.

This composition is prepared by combining and mixing the graft copolymer 1.2 and water, ethanol, sodium hydroxide solution. The remaining ingredients are then added to the mixture.

EXAMPLE 21

The following example represents a topical skin care embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.2	2.00
Water	Q.S. to 100 %
Ethanol (SDA 40)	40.00
Carbomer 940	0.75
Sodium Hydroxide Solution (30% by weight)	0.90
Salicylic Acid	2.00

The composition is prepared by mixing water, ethanol, graft copolymer, and carbomer together for about 10 minutes. The remaining ingredients are added and the mixture is stirred for an additional 30 minutes. This composition is useful for application to the skin to provide improved water resistance and is useful in treating acne.

EXAMPLE 22

The following example represents a nail polish embodiment of the composition of the present invention. The composition is prepared by combining and mixing all of the listed ingredients until uniformly dispersed throughout the composition.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.1	15.00
Ethanol	42.00
Acetone	40.00
NaOH soln., 30%	3.00

EXAMPLE 23

The following example represents a topical skin care embodiment of the composition of the present invention. The topical composition is intended for use in treating, preventing or otherwise reducing the appearance of wrinkles on human skin. The composition is prepared by combining and mixing all of the listed ingredients until uniformly dispersed throughout the composition.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.1	6.00
NaOH soln., 30%	2.10
DRO Water (purified by double reverse osmosis)	q.s.

EXAMPLE 24

The following example represents a hair styling lotion embodiment of the composition of the present invention. The graft copolymer is dissolved in ethanol and then added and mixed with the remaining ingredients until uniformly dispersed throughout the composition.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.1	4.00
Natrosol 250HH ¹	0.50
NaOH soln., 30%	1.35
Kathon CG	0.03
Ethanol	8.00
DRO water	q.s.

¹ Natrosol 250HH-Hydroxyethylcellulose offered by Aqualon.

EXAMPLE 25

The following example represents an aftershave embodiment of the composition of the present invention. The composition is prepared by combining and mixing all of the listed ingredients until uniformly dispersed throughout the composition.

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 1.2	2.00
NaOH soln., 30%	0.60
Ethanol	50.00

Perfume	0.20
Menthol	0.20
DRO water	q.s.

Examples 26-28

The following examples represent hair styling/conditioning rinse embodiments of the compositions of the present invention.

<u>Composition</u>	<u>Example No.</u>		
	<u>26</u>	<u>27</u>	<u>28</u>
<u>Conditioner Premix</u>			
Water	q.s.	q.s.	q.s.
Citric Acid	0.02	0.02	0.02
Sodium Citrate	0.09	0.09	0.10
Cetyl Alcohol	0.12	0.12	0.12
Stearyl Alcohol	0.08	0.08	0.08
Natrosol Plus CS Grade D-67 ¹	1.02	1.00	0.99
Xanthan Gum ²	0.25	0.25	0.25
<u>Styling Polymer Premix</u>			
Graft polymer 2.0	1.75	1.75	1.75
Permethyl 99A	8.54	8.54	8.54
Trimethylsiloxy silicate	0.11	0.11	0.11
Kathon CG	0.03	0.03	0.03
Perfume	0.33	0.33	0.33
<u>Silicone Premix</u>			
DRO Water	9.48	9.48	8.57
Adogen 470 4	0.70	0.60	0.93
Adogen 471 5	0.05	0.15	0.07
Decamethyl cyclopentasiloxane/			
Polydimethyl Siloxane Gum ³	1.67	1.67	2.33
Triethylsilyl Amodimethicone			
(Dow Corning Q2-8220)	0.10	0.10	0.10
<u>Surfactant Premix</u>			
DRO Water	5.70	5.70	5.70
Stearalkonium Chloride	0.30	0.30	0.30

¹Hydrophobically modified hydroxyethyl cellulose from Aqualon Corp.

²Readily dispersible xanthan gum

³SE-76 gum available From General Electric

⁴Ditallow dimethyl ammonium chloride, Sherex Chemical Co., Dublin, Ohio, USA; 75% aqueous solution

⁵Tallow trimethyl ammonium chloride, Sherex Chemical Co.; 50% aqueous solution.

Each of the exemplified compositions are prepared as follows. A silicone premix is prepared by combining and mixing (in a separate vessel) water, Adogen 470 and Adogen 471 at 85°C. Cool to 71°C and add the silicone gum/decamethyl cyclopentasiloxane solution and amodimethicone and mix until homogeneous. Cool to 38°C while using a homogenizer (such as Tekmar). Prepare the surfactant premix by combining and mixing (in a second and separate vessel) water and Stearalkonium Chloride at 38°C. Prepare the conditioner premix by combining and mixing (in a third and separate vessel) DRO water heated to 71°C, citric acid, sodium citrate, cetyl alcohol, stearyl alcohol and Natrosol Plus CS grade D-67, and until uniformly dispersed, and then add xanthan gum and mix until uniformly dispersed. Prepare the styling polymer premix by combining and mixing the graft polymer, permethyl 99A, and Trimethylsiloxy silicate until a uniform mixture is obtained.

Combine and mix the styling polymer premix, Kathon CG and perfume until homogeneous. Further dispersed with an in-line homogenizer (such as Tekmar homogenizer) and then cool the mixture to 38°C. Complete the conditioner by adding the conditioner premix, the silicone premix and the surfactant premix at 38°C. Mix until homogeneous, then cool the composition to 25 °C.

When the compositions defined in Examples 26-28 are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

EXAMPLE 29

Polymer Premix with added Drying Aid

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 2.0	16.83
Permethyl 99A	82.17
Trimethylsiloxy silicate	1.00

This polymer premix is prepared by adding the graft copolymer to the solvents while mixing. The mixture is heated to between 80°C and 84°C in a covered vessel while mixing, and then cooled to between 23°C and 27°C before adding trimethylsiloxy silicate while mixing.

EXAMPLE 30Polymer Premix with added Drying Aid

<u>Ingredients</u>	<u>Weight %</u>
Graft copolymer 2.0	15.00
Isododecane	83.50
Polydimethylsiloxane ²	1.50
² Polydimethylsiloxane, Dow Corning, Dow Corning 200 Fluid (20 csk)	

This polymer premix is prepared by adding the graft copolymer to the solvents while mixing. The mixture is heated to between 80°C and 84°C in a covered vessel while mixing, and then cooled to between 23°C and 27°C before adding trimethylsiloxysilicate while mixing.

EXAMPLE 31

The following example represents a hair conditioning embodiment of the composition of the present invention.

<u>Ingredient</u>	<u>Weight %</u>	<u>A</u>	<u>B</u>
<u>Styling Agent Premix</u>			
Graft copolymer Premix of Example 30	10.00		10.00
<u>Silicone Premix</u>			
Silicone gum, GE SE76 ²	0.30		0.30
Octamethyl cyclotetrasiloxane	1.70		1.70
<u>Main Mix</u>			
Water	QS100	QS100	
Cetyl Alcohol	1.00	---	
Quaternium 18 ³	0.85	0.85	
Stearly Alcohol	0.70	---	
Hydroxethyl Cellulose	0.50	---	
Cetyl Hydroxyethyl Cellulose ⁴	---		
	1.25		
Ceteareth-20	0.35	---	
Fragrance	0.20	0.20	

Dimethicone copolyol	0.20	----
Citric Acid	0.13	0.13
Methylchloroisothiazolinone (and)		
methylisothiazolinone	0.04	0.04
Sodium Chloride	0.01	0.01
Xanthan Gum	----	
	0.20	

Each of the compositions is prepared by comixing all the Main Mix ingredients, heating the resulting mixture to about 60°C with mixing. The heated mixture is then cooled to about 45°C with colloid milling (Example A) or mixing (Example B). At this temperature, the two premixes are added separately with moderate agitation and the resulting conditioner is allowed to cool to room temperature. This composition is useful as a rinse off hair conditioner.

² Commercially available from General Electric.

³ Dimethyl Di(Hydrogenated Tallow) Ammonium Chloride

⁴ Commercially available as Polysurf D-67 from Aqualon.

EXAMPLE 32

The following example represent a shampoo embodiment of the composition of the present invention.

<u>Ingredients</u>	<u>Weight %</u>
<u>Styling Agent</u>	
Copolymer Premix from Example 30	15.00
<u>Premix</u>	
Silicone gum	0.50
Dimethicone, 350 cs fluid	0.50
<u>Main Mix</u>	
Water	QS100
Ammonium lauryl sulfate	11.00
Cocamide MEA	2.00
Ethylene glycol distearate	1.00
Xanthan Gum	1.20
Methylchloroisothiazolinone (and)	

methylisothiazolinone	0.04
Citric Acid to pH 4.5 as needed	

The Main Mix is prepared by first dissolving xanthan gum in water with conventional mixing. The remaining Main Mix ingredients are added and the Main Mix is heated to 150°F with agitation for about 0.5 hour. The Styling Agent and the Premix are then added sequentially with about 10 minutes of agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either or both high shear mixing (high speed dispersator) or normal agitation. This shampoo composition is useful for cleansing the hair and for providing a styling benefit.

What is claimed is:

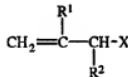
1. Personal care compositions comprising
 - (a) from 0.1% to 15% by weight of a graft polymer made in accordance with the following process steps:
 - (i) reacting copolymerizable monomers to form an organic polymeric backbone having a weight average molecular weight of from 15,000 grams/mole to 9,800,000 grams/mole and a plurality of organic halide moieties covalently bonded to and pendant from the polymeric backbone; and then
 - (ii) reacting copolymerizable monomers with the organic halide moieties of the polymeric backbone by atom transfer free radical polymerization in the presence of a catalytic amount of a Cu(I) salt to form a plurality of polymeric side chains covalently bonded to and pendant from the polymeric backbone, the polymeric side chains having an average molecular weight of from 500 grams/mole to 200,000 grams/mole; wherein the polymeric backbone and the plurality of polymeric side chains form graft polymers having a weight average molecular weight of from 16,000 grams/mole to 10,000,000 grams/mole; and
 - (b) from 0.1% to 99.9% by weight of a liquid carrier.
2. The composition of Claim 1 wherein the graft polymer is hydrophilic and the liquid carrier is selected from the group consisting of water, ethanol, *n*-propanol, isopropanol, and combinations thereof.
3. The composition of any one of the preceding Claims wherein the Cu(I) salts are selected from the group consisting of Cu(I)Br, Cu(I)Cl, Cu(I)I, Cu(I) thiocyanate, and combinations thereof, and wherein the reaction of step (a) is free radical polymerization of the copolymerizable monomers.

4. The composition of any one of the preceding Claims wherein the Cu(I) salt is in the form of a ligand complex, wherein the ligand is an aprotic bidentate selected from the group consisting of 2,2'-dipyridyl, diphosphates, 4,4'-di-5-nonyl-2,2'-bipyridine, 4,4'-di-tert-butylbipyridine, 4,4'-diheptyl-2,2'-bipyridine, and combinations thereof.

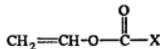
5. The composition of any one of the preceding claims wherein the copolymerizable monomers of step (a) comprise an organic halide-containing vinyl monomer and a second monomer selected from the group consisting of acrylic acid produced by hydrolysis of trimethylsilyl acrylate, methacrylic acid produced by hydrolysis of trimethylsilyl methacrylate, vinyl pyrrolidone, acrylic acid esters of C₁-C₁₈ alcohols, methacrylic acid esters of C₁-C₁₈ alcohols, trimethylsilyl acrylate, trimethylsilyl methacrylate, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts thereof, and mixtures thereof.

6. The composition of Claim 5 wherein the organic halide-containing vinyl monomer of step (a) is selected from the group consisting of

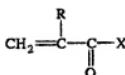
(I)



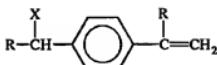
(II)



(III)



(IV)



(V)



and combinations thereof, wherein R is methyl or hydrogen; X is a halogen atom; R, R¹ and R² are each independently methyl, hydrogen or methoxy; and R⁴ is an alkyl group having from 1 to 8 carbon atoms.

7. The composition of any one of the preceding claims wherein the polymeric backbone represents from 50% to 99% by weight of the graft polymer, and the plurality of polymeric side chains represent from 1% to 50% by weight of the graft polymer.

8. The composition of any one of Claims 1, 2, 3 or 4 wherein the graft polymer has a polymeric backbone having a T_g value of less than 10°C and a plurality of polymeric side chains having a T_g value greater than 70°C.

9. The composition of any one of Claims 1, 2, 3 or 4 wherein the graft polymer has a polymeric backbone having a T_g value greater than 50°C and a plurality of polymeric side chains having a T_g value less than -20°C.

10. The composition of any one of Claims 1, 2, 3 or 4 wherein the graft polymer is hydrophobic and the liquid carrier comprises a hydrophobic liquid carrier selected from the group consisting of volatile branched chain hydrocarbons having from 12 to 16 carbon atoms, liquid silicone carriers, and combinations thereof, wherein the liquid silicone carriers are selected from the group consisting of phenyl pentamethyl disiloxane, phenylethyl pentamethyl disiloxane, hexamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, cyclomethicones, including octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 98/00753A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K/00 C08F291/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	WO 95 01383 A (PROCTER & GAMBLE) 12 January 1995 see page 3, line 10-25; claims 1,7-10	1-10

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the international search

8 September 1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

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(54) Title:	TOUGHENED GRAFTED POLYMERS		
(57) Abstract	<p>An adhesive copolymer and personal care composition thereof, said copolymer being characterized by an organic polymeric backbone wherein said backbone has a Tg of from 0 °C to 45 °C wherein said copolymer comprises one or more side chains grafted thereon consisting of acrylic and methacrylic monomer units wherein (each of) said side chains have a Tg of greater than 50 °C-200 °C wherein the number average molecular weight of said side chain is greater than 1000.</p>		

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TOUGHENED GRAFTED POLYMERS
TECHNICAL FIELD

The present invention relates to toughened grafted polymers.

BACKGROUND OF THE INVENTION

5 Cosmetic compositions such as lotions, creams, emulsions, packs, make-up (e.g., foundations, lipsticks, eye shadows and the like) and hair compositions are used to improve one's outward appearance. Many personal care products contain various resins, gums, and adhesive polymers. The polymers are used for a variety of purposes including thickening, feel properties, film-forming ability, active deposition, active penetration, hair holding, etc.

10 Consequently there is constantly a search for developing polymers having improved properties for use in personal care product. For example, the desire to have the hair retain a particular shape is widely held. The most common methodology for accomplishing this is the application of a styling composition to dampened hair, after shampooing and/or conditioning, or to dry, styled hair. These compositions provide temporary setting benefits

15 and they can be removed by water or by shampooing. The materials used in the compositions to provide the setting benefits have generally been resins and have been applied in the form of mousse, gels, lotions or sprays.

Many people desire a high level of style retention, or hold, from a hair spray composition. In typical hair sprays, hold is achieved by the use of resins, such as

20 AMPHOMER[®], supplied by National Starch and Chemical Company, and GANTREZ[®] SP 225, supplied by GAF. In general, as hair hold for hair spray compositions is increased, the tactile feel of the hair becomes stiffer and hence, less desirable. It is desirable to provide hair spray products which could provide an improved combination of hair hold and hair feel characteristics.

25 Recently, it has become known to utilize silicone grafted organic backbone polymers in various personal care compositions including their use as hair setting agents in hairspray compositions and other hair styling compositions, e.g. hair tonics, lotions, rinses, mousse, etc. Silicone grafted polymers can be used to make personal care compositions with improved feel, e.g., in the case of hair sprays, increased softness relative to

30 conventional polymeric hair setting agents.

It remains desirable to improve the performance of grafted polymers. It is an object of this invention to provide toughened graft copolymers which can be used in, for example, personal care compositions.

It is a further object of this invention to provide toughened graft copolymers that

35 have improved adhesive and cohesive properties and low creep at high humidity thereby providing improved style durability benefits.

These and other benefits as may be apparent from the description below can be obtained by the present invention.

The present compositions can comprise, consist of, or consist essentially of any of the required or optional ingredients and/or limitations described herein.

5 All percentages and ratios are calculated on a weight basis unless otherwise indicated. All percentages are calculated based upon the total composition unless otherwise indicated.

10 All ingredient levels refer to the active level of that ingredient, and are exclusive of solvents, by-products, or other impurities that may be present in commercially available sources, unless otherwise indicated.

SUMMARY OF THE INVENTION

The present invention relates to an adhesive copolymer, said copolymer being characterized by an organic polymeric backbone wherein said backbone has a Tg of from about 0°C to about 45°C wherein said copolymer comprises one or more side chains grafted 15 thereon consisting of acrylic and methacrylic monomer units wherein each of said side chains has a Tg of greater than about 50°C - 200°C wherein the number average molecular weight of said side chain is greater than about 1000.

20 By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film or a weld. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are described below. Also included is a nonexclusive description of various optional and preferred components useful in embodiments of the present invention.

25 Grafted Adhesive Polymer

The grafted polymers are characterized by acrylic and methacrylic monomer units covalently bonded to and pendant from a polymeric carbon-based backbone.

30 The backbone will preferably be a carbon chain derived from polymerization of ethylenically unsaturated monomers and wherein said backbone has a Tg of from about 0°C to about 45° C.

35 The grafted polymer should have a weight average molecular weight of at least about 20,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between

about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 80,000 and about 750,000.

The term "graft copolymers" is familiar to one of ordinary skill in polymer science and is used herein to describe the copolymers which result by adding or "grafting" polymeric side 5 chain moieties (i.e. "grafts") onto another polymeric moiety referred to as the "backbone". The backbone typically has a higher molecular weight than the grafts. Thus, graft copolymers can be described as polymers having pendant polymeric side chains, and as being formed from the "grafting" or incorporation of polymeric side chains onto or into a polymer backbone. The polymer backbone can be a homopolymer or a copolymer. The 10 graft copolymers are derived from a variety of monomer units.

The graft polymers made in accordance with the methods herein can have a single Tg and preferably are copolymers having at least two distinct immiscible phases, wherein the polymeric side chains are closely associated with each other and exist in one phase and polymeric backbone of the copolymer remains in a second separate phase. A consequence 15 of this phase immiscibility is that if the temperature separation between each of the Tg's values involved is large enough then these copolymers exhibit two distinct Tg's, namely one Tg value for the backbone and one Tg value for the side chain. The term Tg means glass transition temperature, which is familiar to one of ordinary skill in the art. The copolymers can also exhibit a third glass transition temperature corresponding to any optional 20 polysiloxane side chains on the graft copolymers. Whether such a third Tg value is observable depends upon a number of factors including the percent silicone in the copolymer, the number of polysiloxane side chains in the copolymer, the temperature separation between each of the Tg's values involved, and other such physical factors.

Backbone Vinyl Monomer Units:

25 The copolymers of the present invention comprise from about 50% to about 98%, preferably from about 60% to about 95%, and more preferably from about 70% to about 90% by weight of the backbone vinyl monomer units.

The backbone vinyl monomer unit is selected from copolymerizable monomers, preferably ethylenically unsaturated monomers. The monomers are selected to meet the 30 requirements of the copolymer. By "copolymerizable", as used herein, is meant that the vinyl monomer can be reacted with or polymerized with the acrylic or methacrylic macromonomers in a polymerization reaction using one or more conventional synthetic techniques, such as ionic, emulsion, dispersion, Ziegler-Natta, free radical, group transfer or step growth polymerization. In the present invention, monomers and macromonomers that 35 are copolymerizable using conventional free radical initiated techniques are preferred. The term "ethylenically unsaturated" is used herein to mean a material that contains at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri- or tetra-substituted.

The monomer units can be derived from hydrophilic monomers (typically polar monomers), or mixtures of such hydrophilic monomers with hydrophobic monomers (typically low polarity monomers), provided that the solubility characteristics of the overall copolymer is achieved. As used herein, "hydrophilic monomers" means monomers which

5 form homopolymers which are substantially water soluble; "hydrophobic monomers" means monomers which form substantially water insoluble homopolymers.

Preferred monomers include unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated 10 monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of 15 unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.

More preferred monomer units are selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized 20 dimethylaminoethyl methacrylate, vinyl pyrrolidone, C₁-C₁₈ alkyl esters of acrylic or methacrylic acid, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride, vinyl toluene, 2-methoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and 25 combinations thereof.

Most preferred monomer units of said backbone (i) selected from the group consisting of acrylic acid, methacrylic acid, 2-methoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate and mixtures thereof.

30 The backbone has a Tg of from about 0° C to about 45° C, preferably from about 0° C to about 35° C, and most preferably from about 0° C to about 25° C.

Acrylic and Methacrylic Acid Macromonomer Side Chain Units

The copolymers of the present invention comprise from about 2% to about 50%, preferably from about 5% to about 40%, and more preferably from about 10% to about 30%, 35 by weight of the copolymer of acrylic and methacrylic macromonomer side chain units.

The macromonomer units are copolymerizable with the vinyl monomers, said macromonomers preferably having a vinyl moiety. Either a single type of macromonomer

unit or combinations or two or more macromonomer units can be utilized herein. The macromonomers are selected to meet the requirements of the copolymer. By "copolymizable", as used herein, is meant that the macromonomers can be reacted with or polymerized with the vinyl monomers in a polymerization reaction using one or more conventional synthetic techniques, as described above.

5 The macromonomers that are useful herein contain a polymeric portion and a copolymerizable moiety which is preferably an ethylenically unsaturated moiety. Typically, the preferred macromonomers are those that are endcapped with the vinyl moiety. By "endcapped" as used herein is meant that the vinyl moiety is at or near a terminal position of 10 the macromonomer.

10 The macromonomers can be synthesized utilizing a variety of standard synthetic procedures familiar to the polymer chemist of ordinary skill in the art. Furthermore, these macromonomers can be synthesized starting from commercially-available polymers. Typically, the weight average molecular weight of the macromonomer is from about 1000 to 15 about 50,000.

15 Preferred macromonomers are poly(acrylate) and polymethacrylate) macromonomers. Macromonomers are exemplified by the general formula:



20 wherein I is an optionally present initiator (i.e. n = 0 or 1), W is a monomer unit, E is an endcapping group, and m is an integer from about 10 to about 2000.

25 I is an optionally present chemical initiator moiety. Without being limited by theory, I can be derived from a chemical initiator or solvent used in the synthesis of the macromonomer. Nonlimiting examples of such initiators from which I can be derived include hydrogen ion, hydrogen radical, hydride ion, hydroxide ion, hydroxyl radical, peroxide radical, peroxide anion, C₁-C₂₀ carbocations, C₁-C₂₀ carbanions, C₁-C₂₀ carbon radicals, C₁-C₂₀ aliphatic and aromatic alkoxy anions, ammonium ion, and substituted ammonium ions (e.g., C₁-C₂₀ alkyl and C₁-C₂₀ alkoxy substituted), and mixtures thereof. I can be derived from any useful solvent, nonlimiting examples of which include water, methanol, ethanol, propanol, isopropanol, acetone, hexane, dichloromethane, chloroform, benzene, 30 toluene, and mixtures thereof.

W is selected from the group consisting of an acrylic acid monomer unit, a methacrylic acid monomer unit and mixtures thereof. Nonlimiting classes of such monomers include C₁-C₁₈ straight and branched chain acrylate esters and C₁-C₁₈ straight and branched chain methacrylate esters, and mixtures thereof.

35 Preferably the monomer units of the side chains are selected from the group consisting of acrylic acid (produced by hydrolysis of trimethylsilyl acrylate), methacrylic acid (produced by hydrolysis of trimethylsilyl methacrylate), phenyl methacrylate, benzyl

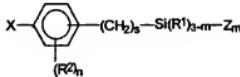
methacrylate, and C₁-C₁₈ alkyl esters of acrylic or methacrylic acid and mixtures thereof. More preferably, the monomer units are selected from the group consisting acrylic acid (preferably produced by hydrolysis of trimethylsilyl acrylate), methacrylic acid (preferably produced by hydrolysis of trimethylsilyl acrylate), n-propyl methacrylate, iso-butyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, 2-hydroxyethyl methacrylate (produced by hydrolysis of trimethylsilyl protected alcohol), 2-hydroxypropyl methacrylate (produced by hydrolysis of trimethylsilyl protected alcohol). Most preferred are monomer units of selected from the group consisting of acrylic acid (preferably produced by hydrolysis of trimethylsilyl acrylate), methacrylic acid (preferably produced by hydrolysis of trimethylsilyl acrylate), n-propyl methacrylate, iso-butyl methacrylate and mixtures thereof.

Each side chain has a T_g of from about 50°C to about 200°C, preferably of from about 60°C to about 150°C and most preferably of from about 70°C to about 110°C.

Optionally, the adhesive copolymers can further comprise one or more polysiloxane macromonomer side chains exemplified by the general formula:

15 X(Y)_nSi(R)_{3-m}Z_m
 wherein X is a vinyl group copolymerizable with the vinyl monomer units; Y is a divalent linking group; each R is independently selected from the group consisting of hydrogen, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, C₂-C₆ alkylamino, phenyl, C₁-C₆ alkyl or alkoxy-substituted phenyl; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. The polysiloxane macromonomer has a weight average molecular weight from about 1000 to about 50,000, preferably from about 5,000 to about 30,000, more preferably from about 8,000 to about 25,000.

25 Preferably, the polysiloxane macromonomer has a formula selected from the following formulas:



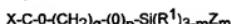
or



30 or

0

||



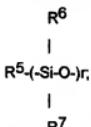
In these structures s is an integer from 0 to 6; preferably 0, 1, or 2; more preferably 0 or 1; m is an integer from 1 to 3, preferably 1; p is 0 or 1; q is an integer from 2 to 6; each R¹ is

independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, preferably C1-C6 alkyl, or C1-C6 alkyl or alkoxy-substituted phenyl, more preferably C1-C6 alkyl, even more preferably methyl. R² is selected from the group consisting of C1-C6 alkyl or C1-C6 alkyl substituted phenyl, preferably methyl.

5 n is an integer from 0 to 4, preferably 0 or 1, more preferably 0; X is



10 wherein R³ is hydrogen or -COOH, preferably R³ is hydrogen; R⁴ is hydrogen, methyl or -CH₂COOH, preferably R⁴ is methyl; Z is



15 wherein R⁵, R⁶, and R⁷, are independently selected from hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, hydrogen or hydroxyl, preferably R⁵, R⁶, and R⁷ are C1-C6 alkyls; more preferably methyl; 20 and r is an integer of from about 14 to about 700, preferably about 60 to about 400, and more preferably about 100 to about 350.

Exemplary grafted polymers for use in the present invention include the following, where the composition is given as weight part of monomer used in the synthesis:

- (i) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)-graft-25 poly (n-propyl methacrylate-co-methacrylic acid)
MW of copolymer: 149,900
Backbone: 80 %
Backbone Composition: t-butyl acrylate (53%), 2-methoxyethyl acrylate (36%), methacrylic acid (11%)
- 30 Macromonomer side chains: 20 %
Macromonomer side chains Composition: n-propyl methacrylate (65%); methacrylic acid (35%)
Macromonomer side chains MW: 6,000
- (ii) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)-graft-35 poly (iso-butyl methacrylate-co-methacrylic acid)
MW of copolymer: 55,000
Backbone: 80 %

Backbone Composition: t-butyl acrylate (53%), 2-methoxyethyl acrylate (36%), methacrylic acid (11%)
Macromonomer side chains: 20%

5 Macromonomer side chains Composition: iso-butyl methacrylate (65%); methacrylic acid (35%)
MW_n of Macromonomer side chains: 8,000
(iii) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-[poly (n-propyl methacrylate-co-methacrylic acid); poly(dimethylsiloxane)]
MW_n of copolymer: 83,000
10 Backbone: 77 %
Backbone Composition: t-butyl acrylate (43%), 2-methoxyethyl acrylate (38%), acrylic acid (18%)
Macromonomer side chains: 17%
Macromonomer side chains Composition: n-propyl methacrylate (60%); methacrylic acid (40%)
15 MW_n of Macromonomer side chains: 6,000
Poly(dimethylsiloxane) macromonomer side chains: 6%
MW_n of poly(dimethylsiloxane): 10,000
(iii) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-[poly (n-propyl methacrylate-co-methacrylic acid); poly(dimethylsiloxane)]
20 MW_n of copolymer: 150,000
Backbone: 77 %
Backbone Composition: t-butyl acrylate (43%), 2-methoxyethyl acrylate (38%), acrylic acid (18%)
25 Macromonomer side chains: 20%
Macromonomer side chains Composition: n-propyl methacrylate (60%); methacrylic acid (40%)
MW_n of Macromonomer side chains: 10,000
Poly(dimethylsiloxane) macromonomer side chains: 3%
30 MW_n of poly(dimethylsiloxane): 10,000

The copolymers of the present invention are prepared by the polymerization combination of vinyl monomers and macromonomers. The copolymers can be synthesized by free radical polymerization of the monomers and macromonomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 3rd edition, John Wiley & Sons, 1991, pp. 198-334, incorporated by reference herein. The desired vinyl monomers and macromonomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the

reaction is complete the viscosity of the reaction is reasonable. Undesired terminators, especially oxygen, are removed as needed. This can be done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The copolymer can be further purified, as desired.

10 As an alternative to a batch reaction, the copolymer can be made by a semi-continuous or continuous process. In the semi-continuous process, two or more additions of monomers or macromonomers are made during the polymerization reaction. This is advantageous when the copolymer is made of several monomers which react during the polymerization at different rates. The proportions of monomers added to the reaction at the 15 separate points of addition can be adjusted by one of ordinary skill in the art such that the polymers of the final product have a more uniform structure. In other words, the polymers of the final product will have a more consistent monomer content distribution for each of the monomer types charged to the reaction.

20 The copolymers are prepared by the polymerization combination of vinyl monomers and macromonomers. The copolymer composition is characterized by the amount of each monomer charged to the polymerization reaction vessel, or alternatively used in a continuous or semi-continuous process.

25 By appropriate selection and combination of the particular vinyl monomer units and macromonomer units, and by the choice of specific relative ratios of the units well within the ability of one of ordinary skill in the art, the copolymers can be optimized for various physical properties and for compatibility with other ingredients commonly used in hair care applications.

30 As is be clear to one skilled in the art, the copolymer may have one or more side chains grafted to the backbone. In addition, the polymers of the present invention can be used alone or in addition to the copolymer, low levels of the corresponding copolymers having no side chains grafted to the backbone. As known in the art, synthetic graft copolymerization processes may produce a mixture of polymer molecules containing none, one, or more than one side chains covalently bonded to and pendant from the polymeric backbone. From knowledge of the amount and number average molecular weight of side 35 chains in a polymer sample, and the number average molecular weight of the polymer sample, it is possible to calculate the average number of side chains per polymer backbone.

Optional Components

The copolymers of the present invention can be formulated into personal care compositions, or any other composition in which an adhesive polymer may be useful such as adhesive tapes, glues, and the like. Personal care compositions comprise from about 0.1% to about 99%, preferably from 0.5% to about 50%, more preferably from about 1% to 5 about 10%, by weight of the composition, of the grafted polymer and from about 0.1% to about 99.9%, preferably from about 0.5% to about 99.0% and most preferably from about 1.0% to about 99.9% of a suitable personal care carrier. Solvents are preferably selected from the group consisting of water, ethanol, *n*-propanol, isopropanol, and mixtures thereof. The polymers are soluble at a concentration of at least about 0.1 mg/mL, preferably at least 10 about 0.5 mg/mL, and more preferably at least about 1 mg/mL, at about 25°C.

The graft polymers made in accordance with the synthesis methods herein may have acidic functionalities, such as carboxyl groups, and are usually used in at least partially neutralized form to promote solubility/dispersability of the polymer. In addition, use of the neutralized form aids in the ability of the hair styling compositions to be removed from the 15 hair by shampooing. The extent of such neutralization ranges from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about 40% to about 85%, neutralization of the acidic functionalities of the graft polymer.

Neutralization of the graft polymers containing acidic functionalities may be 20 accomplished by any conventional or otherwise known technique for effecting such neutralization of by using an organic or inorganic base material. Metallic bases are particularly useful for this purpose. Suitable base neutralizers include, but are not limited to, ammonium hydroxides, alkali metal hydroxides, or an alkaline earth metal hydroxides, preferably potassium hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents include, but are not limited to, amines or amino alcohols such as 25 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA) and dimethyl stearamine (DMS). Preferred are amines and metallic bases.

Neutralization of graft polymers containing basic functionalities, e.g., amino groups, 30 are likewise preferably at least partially neutralized with an organic or inorganic acid e.g., hydrogen chloride. Neutralization can be accomplished by any conventional or otherwise known technique for accomplishing such neutralization. The preferred extent of neutralization is the same as that described for neutralization of acidic functionalities. 35 Solubility for any neutralized graft polymers made in accordance with the method herein should be determined only after the desired acid or base neutralization.

The solvents that are present in hair care compositions are at a level of from about 80% to about 99%, preferably from about 85% to about 98%, more preferably from about 90% to about 95% of the total composition.

The solvents essential to such compositions are selected from the group consisting of water, C₂-C₃ monohydric alkanols, and mixtures thereof. If present, C₃ alkanols, such as isopropanol, should be used at levels no greater than about 15% by weight of the composition, preferably no greater than about 12%, more preferably no greater than about 10%. High levels of C₃ monohydric alcohols are undesirable in the present compositions due to potential odor issues they can create. Preferred polar solvent phases contain water, ethanol, or mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50% by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the range of from 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the total composition.

In yet another aspect of this invention are provided hair styling products, such as hair spray compositions, which contain reduced levels of volatile organic solvents. A reduced volatile organic solvent hair spray composition of the present invention contains no more than 80% volatile organic solvents (which include, for example, alkanols but not water). As used herein, volatile organic solvents means solvents which have at least one carbon atom and exhibit a vapor pressure of greater than 0.1 mm Hg at 20°C.

In reduced volatile organic solvent hair styling products, the compositions generally comprise at least 10%, by weight, of water. It is also specifically contemplated that they 25 may contain at least about 11%, 12%, 13%, 14%, 15%, or more water.

The reduced volatile organic solvent compositions hereof will comprise up to about 90%, preferably up to about 70%, more preferably up to about 60% even more preferably no more than about 50%, water; and from about 10% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 80%, of volatile organic solvent. It is 30 also contemplated that the compositions can be limited to containing no more than about 75%, 65%, 55%, or other levels of volatile organic solvents.

In addition the compositions could contain branched chain hydrocarbon solvent present at a level of from about 0.1% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 2% to about 8%, by weight of the composition. Also useful 35 are low boiling point silicone oils.

The branched chain hydrocarbon solvent is characterized by a boiling point of at least about 105°C, preferably at least about 110°C, more preferably at least about 125°C,

most preferably at least about 150°C. The boiling point is also generally about 260°C or less, preferably about 200°C or less. The hydrocarbon chosen should also be safe for topical application to the hair and skin.

The branched chain hydrocarbon solvents are selected from the group consisting of 5 C₁₀-C₁₄ branched chain hydrocarbons, and mixtures thereof, preferably C₁₁-C₁₃ branched chain hydrocarbons, more preferably C₁₂ branched chain hydrocarbons. Saturated hydrocarbons are preferred, although it is not necessarily intended to exclude unsaturated hydrocarbons.

Examples of suitable nonpolar solvents include isoparaffins of the above chain 10 sizes. Isoparaffins are commercially available from Exxon Chemical Co. Examples include Isopar™ G (C₁₀-C₁₁ isoparaffins), Isopar™ H and K (C₁₁-C₁₂ isoparaffins), and Isopar™ L (C₁₁-C₁₃ isoparaffins). The most preferred nonpolar solvent are C₁₂ branched chain hydrocarbons, especially isododecane. Isododecane is commercially available from Preperse, Inc. (South Plainfield, NJ, USA) as Permethyl™ 99A.

15 **Plasticizer**

The compositions hereof can optionally contain a plasticizer for the grafted polymer. Any plasticizer suitable for use in hair care products or for topical application to the hair or skin can be used. A wide variety of plasticizers are known in the art. These include acetyl triethylcitrate, triethylcitrate, glycerin, diisobutyl adipate, butyl stearate, and propylene glycol. 20 Plasticizers are typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%.

Additional Adhesive Polymer

The adhesive polymers of the present invention can be used in combination with an 25 additional adhesive polymer. The compositions hereof will generally comprise from about 0.1% to about 15%, preferably from 0.5% to about 8%, more preferably from about 1% to about 8%, by weight of the composition, of the adhesive polymer. It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive or film-forming properties to the composition and the composition 30 can be formulated and effectively applied for its intended purpose. By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

The polymeric backbone is chosen such that it is compatible with the adhesive 35 styling polymer. By "compatible" is meant is that, when placed in a suitable solvent, the polymers form a stable solution, i. e., the polymers do not compete for solubility and therefore, cause no phase separation and when the solution is dried a uniform film is formed,

with no macrophase separation of the two polymers. A suitable solvent is a solvent which substantially completely dissolves the non-silicone and silicone grafted polymers at the levels described herein. The polymer blend forms a relatively clear hairspray system (% transmittance at 450 nm is generally greater than 80%). It is recognized that certain 5 plasticizers can form cloudy films as well as incorrect neutralization levels. Therefore, this would fall outside this definition of compatibility. The compatibility can be tested by dissolving the polymers in a mutual solvent, and then evaporating the solvent to form a film. Incompatible polymers will form a cloudy film with poor mechanical properties, due to the large scale phase separation of the two polymers. Although compatibility can occur between 10 two polymers of completely different structures, it is preferred that compatibility be obtained by making the composition of the respective backbones similar to or identical to one another.

The adhesive polymer should have a weight average molecular weight of at least about 20,000, preferably greater than about 25,000, more preferably greater than about 15 30,000, most preferably greater than about 35,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 2,000,000. Preferably, the weight average molecular weight will be between about 20,000 and about 2,000,000, more preferably 20 between about 30,000 and about 1,000,000, and most preferably between about 40,000 and about 500,000.

Preferably the weight ratio of the toughened graft polymer of the present invention to adhesive polymer ranges from about 1:10 to about 1:1, preferably from about 1:5 to about 1:1.

25 Exemplary adhesive polymers for use in the present invention include the following, where the numbers following the structure indicate the weight ratios of monomers as loaded into the polymerization reactor:

- (i) acrylic acid/t-butyl acrylate 25/75
- (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-30 -ethylhexyl-methacrylate 40/40/20
- (iii) t-butylacrylate/acrylic acid 65/35
- (iv) polymer (ii) quaternized by treatment with methyl chloride

The adhesive polymers can be synthesized as described above such as by free radical polymerization of the monomers.

35 Solubility of the adhesive polymer, as described above, should be determined after neutralization, if any, as well as after addition of other ingredients that may be included in the polar solvent phase, such as surfactants, solubilizers, etc.

The present compositions can contain a wide variety of additional optional ingredients, including among them any of the types of ingredients known in the art for use in hair setting compositions, especially hair spray compositions and hair setting tonics. These ingredients include, but are not limited to, surfactants (including fluorinated surfactants and 5 silicone copolymers), and ionic strength modifiers, propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.)

Ionic Strength Modifier System

10 Optionally, the compositions can contain an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the hair spray composition. When used, the ionic strength modifiers will be present in the present compositions at a level of at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or 15 dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the polar liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for 20 example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, 25 more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface 30 tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

35 The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH⁻ and H⁺ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they

can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures 5 of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. 10 Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below.

15 Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, 20 bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts 25 which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The use of ionic strength modifiers are especially useful in reduced volatile organic solvent compositions, most especially those utilizing silicone macromer-containing 30 polymers.

Personal Care Compositions

The adhesive polymers of the present invention can be used in a wide variety of personal care compositions, including shampoos, soaps, lotions, creams, antiperspirants, 35 nail enamels, lipsticks, foundations, mascaras, sunscreens, hair spray compositions, mousses, and hair setting tonics. Compositions that will be flowable, e.g., low viscosity

compositions that, preferably, are suitable for spray application as well as higher viscosity compositions are also contemplated.

Personal care carriers are suitable for use in the present invention are described in U.S. Patent 5,306,485 to Robinson et al., issued April 26, 1994, and U.S. Patent 5,002,680 to Schmidt et al., issued March 26, 1991, both of which are incorporated by reference herein. Hair spray compositions and mousses of the present invention can be dispensed from containers which are aerosol dispensers or pump spray dispensers. Such dispensers, i.e., containers, are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants may be used to propel the compositions. A suitable propellant for use can be generally any liquefiable gas conventionally used for aerosol containers.

Suitable propellants for use are volatile hydrocarbon propellants which can include liquefied lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, N-butane, isobutane, propanes, nitrogen, carbon dioxide, nitrous oxide and atmospheric gas and mixtures thereof.

The aerosol propellant may be mixed with the present compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquefiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 40% by weight of the total composition.

Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other hair styling compositions include tonics and lotions, which are typically dispensed in a conventional bottle or tube, and applied directly to the hair or first dispensed to the hand and then to the hair.

The hair styling formulations of the present invention can optionally contain

5 conventional hair care composition adjuvants. Generally, adjuvants collectively can comprise from about 0.05% to about 5% by weight and preferably from about 0.1% to about 3%, by weight. Such conventional optional adjuvants are well known to those skilled in the art and include in addition to those discussed above, emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives;

10 ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents; sunscreens; preservatives; thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

The personal care compositions of the present invention can be made using conventional formulation and mixing techniques.

15 The compositions of the present invention are used in conventional ways to provide the personal care compositions of the present invention. Such method generally involves application of an effective amount of the product. For example, in a hair spray composition, said composition is applied to the desired dry, slightly damp, or wet hair before and/or after the hair is arranged to a desired style. The composition is then dried or allowed to dry. By

20 "effective amount" is meant an amount sufficient to provide the desired benefits.

The following Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

25 **EXAMPLES**

The following synthesis exemplify grafted polymers useful in the present compositions.

Synthesis of para-vinyl benzoyl chloride

To a clean round bottom flask with an argon atmosphere and equipped with a magnetic stir bar is added para-vinyl benzoic acid (10 g, 0.067 mole) which is suspended in benzene (25 ml). Oxalyl chloride (25 g, 0.197 mole) is added to the flask. The mixture is stirred for 8 hours and continuously flushed with a continuous stream of argon to purge the system of the gases generated during the reaction. Solvent and excess oxalyl chloride is stripped off under vacuum. Finally, the product is distilled under vacuum to yield para-vinyl benzoyl chloride.

30

35 Approximately 90% of the theoretical yield is obtained.

Synthesis of Vinylphenyl-terminated Poly(n-propyl methacrylate-co-methacrylic acid) Macromonomer

Into a round-bottomed-flask fitted with a magnetic stirring and under slight argon pressure (8 psi), is added tetrahydrofuran (1L), trimethylsilylmethacrylate (100g, 0.632 mole), and n-propylmethacrylate (100g, 0.780 mole). The solution is cooled to -80°C then initiated with diphenylhexylolithium (0.0275 moles) (prepared by adding 1:1 mole ratio of sec-5 butyl lithium and 1,1-diphenyl ethylene in THF) for chain propagation via anionic polymerization mechanism. After continuous stirring for 0.5 hours, vinylbenzoyl chloride (8.33 mL, 0.05 mole) is charged to the solution and continued stirring for 0.5 hours. The solution is then warmed to ambient temperature and H₂O (10mL) is added and stirred for 0.25 hours to deprotect the acid groups. The macromonomer, which has a weight average 10 molecular weight of about 6000, is obtained by precipitating the resulting solution in hexanes, collecting precipitate, and drying under vacuum.

Example 1

Synthesis of Poly(t-butylacrylate-co-2-methoxyethylacrylate-co-acrylic acid)-graft-[poly(n-propyl methacrylate-co-methacrylic Acid);poly(dimethylsiloxane)] Copolymer

15 To a round-bottomed-flask equipped with a reflux condenser, temperature control, mechanical stirring mechanism, and under slight argon pressure (8psi), is added acetone (0.5L), t-butylacrylate (22.3g), 2-methoxyethylacrylate (36g), acrylic acid (18g), poly(dimethylsiloxane) macromonomer (6g) (Chisso Corp. Tokyo, Japan), and vinylphenyl-terminated (n-propylmethacrylate-co-methacrylic acid) macromonomer (18g) (from Example 20). Solution is stirred until all components are dissolved, then heated to 60°C. Azobisisobutyronitrile (0.7g) is charged to the system. After 10 hours, solution is cooled and precipitated in water to yield silicone modified graft copolymer.

Example 2

Synthesis of Poly(t-butylacrylate-co-2-methoxyethylacrylate-co-methacrylic acid)-graft-[poly(n-propyl methacrylate-co-methacrylic Acid) Copolymer

25 To a round-bottomed-flask equipped with a reflux condenser, temperature control, mechanical stirring mechanism, and under slight argon pressure (8psi), is added acetone (0.5L), t-butylacrylate (42.4 g), 2-methoxyethyl acrylate (29g), methacrylic acid (9g), and vinylphenyl-terminated (n-propylmethacrylate-co-methacrylic acid) macromonomer (20g) (from Example 30). Solution is stirred until all components are dissolved, then heated to 60°C. Azobisisobutyronitrile (0.5g) is charged to the system. After 10 hours, solution is cooled and precipitated in water to yield the graft copolymer.

CLAIMS:

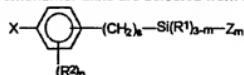
1. An adhesive copolymer, said copolymer being characterized by an organic polymeric backbone wherein said backbone has a Tg of from 0°C to 45°C wherein said copolymer comprises one or more side chains grafted thereon consisting of acrylic and methacrylic monomer units wherein [each of] said side chains have a Tg of greater than 50°C -200°C wherein the number average molecular weight of said side chain is greater than 1000.
2. An adhesive copolymer according to claim 1, wherein said backbone monomer unit is selected from the group consisting of unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated dicarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.
3. An adhesive copolymer according to claim 2, wherein said backbone monomer unit is selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, C₁-C₁₈ alkyl esters of acrylic or methacrylic acid, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride, vinyl toluene, 2-methoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and combinations thereof, wherein the backbone of has a Tg of from 0° C to 45° C.
4. An adhesive copolymer according to claim 1, wherein said side chain has general formula:



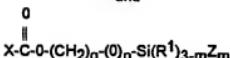
wherein I is an initiator, n = 0 or 1, W is a monomer unit from the group consisting of an acrylic acid monomer unit, a methacrylic acid monomer unit and mixtures thereof, E is an endcapping group, and m is an integer from 10 to 2000.

5. A personal care composition according to claim 4, wherein said monomer unit of said side chain is selected from the group consisting of an acrylic acid monomer unit, a methacrylic acid monomer unit and mixtures thereof. Nonlimiting classes of such monomers include C₁-C₁₈ straight and branched chain acrylate esters and C₁-C₁₈ straight and branched chain methacrylate esters, and mixtures thereof.
6. A personal care composition according to claim 5, wherein said monomer unit of each of said side chains is selected from the monomer units are selected from the group consisting acrylic acid, methacrylic acid, n-propyl methacrylate, iso-butyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate.
7. A personal care composition according to claim 6, wherein said monomer units of each of said side chains is selected from the group consisting of acrylic acid, methacrylic acid, n-propyl methacrylate, iso-butyl methacrylate and mixtures thereof, wherein each side chain of said polymer has a Tg of from 50° C to 200° C.
8. An adhesive copolymer according to claim 1, wherein said backbone further comprises one or more side chains having a polysiloxane-containing macromonomer units, wherein said polysiloxane-containing macromonomer side chains have a weight average molecular weight from 1,000 to 50,000, and correspond to the chemical formula:
$$X(Y_nSi(R)_{3-m}Z)_m$$
 wherein:
X is a vinyl group copolymerizable with said vinyl monomer units;
Y is a divalent linking group;
R is selected from the group consisting of hydrogen, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, C₂-C₆ alkylamino, phenyl, C₁-C₆ alky or alkoxy-substituted phenyl;
Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 1000, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization;
n is 0 or 1; and
m is an integer from 1 to 3.

9. A An adhesive copolymer according to Claim 8 wherein said polysiloxane-containing macromonomer units are selected from the group consisting of:



and



wherein s is 0, 1, 2, 3, 4, 5 or 6; m is 1, 2 or 3; p is 0; q is 2, 3, 4, 5 or 6; R^1 is selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, R^2 is selected from the group consisting of C1-C6 alkyl or C1-C6 alkyl substituted phenyl; n is 0, 1, 2, 3 or 4; X is

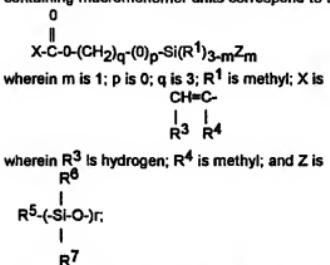


wherein R^3 is hydrogen or $-\text{COOH}$; R^4 is hydrogen, methyl or $-\text{CH}_2\text{COOH}$; Z is

$$\begin{array}{c}
 \text{R}^6 \\
 | \\
 \text{R}^5 - (\text{Si}-\text{O}-)^r \\
 | \\
 \text{R}^7
 \end{array}$$

R^5 , R^6 , and R^7 independently are independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, and r is an integer of from 14 to 700.

10. A An adhesive copolymer according to Claim 9 wherein said polysiloxane-containing macromonomer units correspond to the chemical formula:



R^5 , R^6 , and R^7 are independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, and r is an integer of from 14 to 700.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 98/00702A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09J151/00 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09J COBF A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 981 902 A (MITRA SMARAJIT ET AL) 1 January 1991 see column 5, line 61-66	1-10
X	EP 0 491 169 A (LINTEC CORP) 24 June 1992 see page 5, line 4-15 see page 5, line 50-53	1-10
P, X	EP 0 815 848 A (OREAL) 7 January 1998 see the whole document	1-7
X	EP 0 357 229 A (DU PONT) 7 March 1990 see page 4, line 13-49; claims 1,4	1-4

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

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"S" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 98/00702

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